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**Telegraphic Address.**—“IROSAMENTE, SOWEST, LONDON.”

**Telephone.**—SLOANE 0061.

## PREFACE.

THE present volume contains twenty-seven papers presented at the Annual General Meeting of the Institute held in London on May 11th, 1944; of these, twelve papers were presented under the auspices of the Joint Research Committees of the Institute and the British Iron and Steel Federation. The discussion and correspondence on these papers are also included, together with the authors' replies. In addition, further discussion on the Fourth Report of the Oxygen Sub-Committee, together with the Sub-Committee's reply, will be found in the present book, and also a publication notice of Special Report No. 29, "Review of the Work of the Joint Research Committees, 1924-1943, of The Iron and Steel Institute and The British Iron and Steel Federation reporting to the Iron and Steel Industrial Research Council." In February, 1944, a booklet on "The Training of Metallurgists" was issued by authority of the Council, and this also is included in the pages of the present volume.

Section I. of this volume contains the above-mentioned material and also the Minutes of the Proceedings of the Meeting, including the Report of Council and Statement of Accounts for 1943, and the Presidential Address.

Section II. is devoted to a survey of the literature of the manufacture and properties of iron and steel, and kindred subjects, and consists of a collection of abstracts of articles from the Transactions and Proceedings of scientific societies and from the technical press. This section also contains reviews of recent books and bibliographies of literature dealing with the manufacture and properties of iron and steel. The matter included in this Section has already appeared in the *Bulletin of The Iron and Steel Institute*, which is issued monthly.

In front of the title-page are inserted lists of Bibliographies and Special Reports issued by the Institute, together with a list of Translations made available from the beginning of the year.

4, GROSVENOR GARDENS,  
LONDON, S.W. 1.  
November 20th, 1944.

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## ABBREVIATIONS USED IN THE TEXT.

Å.	Angström unit(s).	kg.cal.	kilogramme-calory,
A.C.	air-cooled; alternating current.	kg.m.	-calories.
A.H.	air-hardened.	km.	kilogramme-metre(s).
amp.	ampère(s).	kVA.	kilometre(s).
amp.hr.	ampère-hour(s).	kW.	kilovolt-ampère(s).
atm.	atmosphere(s) (pressure).	kWh.	kilowatt(s).
Bé.	Baumé (scale).	lb.	kilowatt-hour(s).
b.h.p.	brake horse-power.	L.F.	pound(s).
B.O.T.	Board of Trade.	m.	low-frequency.
B.Th.U.	British thermal unit(s).	m.amp.	metre(s).
C.	centigrade (scale).	mV.	milliampère(s).
cal.	calory, calories.	max.	millivolt(s).
c.c.	cubic centimetre(s).	mg.	maximum.
c.d.	current density.	min.	milligramme(s).
c.g.s.	centimetre-gramme-second unit(s).	ml.	minimum; minute(s).
cm.	centimetre(s).	mm.	millilitre(s).
coeff.	coefficient.	m.m.f.	millimetre(s).
const.	constant(s).	N.	magnetomotive force.
c.p.	candle-power.	N.T.P.	normal (solution).
cu.	cubic.	O.H.	normal temperature and pressure.
cwt.	hundredweight(s).	O.Q.	open-hearth; oil-hardened.
D.C.	direct current.	oz.	oil-quenched.
dia.	diameter.	p.d.	ounce(s).
dm.	decimetre(s).	pH	potential difference.
e.m.f.	electromotive force.	r.p.m.	hydrogen-ion concentration.
F.	Fahrenheit (scale).	sec.	revolutions per minute.
ft.	foot, feet.	sp. gr.	second(s).
ft.lb.	foot-pound(s).	sq.	specific gravity.
g.	gramme(s).	T.	square.
gal.	gallon(s).	temp.	tempered.
H.F.	high-frequency.	V.	temperature.
h.p.	horse-power.	V.A.	volt(s).
h.p.hr.	horse-power-hour(s).	Wh.	volt-ampère(s).
hr.	hour(s).	W.G.	watt-hour(s).
in.	inch, inches.	W.Q.	water gauge.
in.lb.	inch-pound(s).	yd.	water-quenched.
K.	absolute temperature (Kelvin scale),	°	yard(s).
kg.	kilogramme(s).		degree(s).

SECTION I.

*MINUTES OF PROCEEDINGS  
AND PAPERS OF  
THE IRON AND STEEL INSTITUTE.*

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ANNUAL MEETING  
1944

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MINUTES OF PROCEEDINGS  
AND  
PAPERS AND DISCUSSIONS  
AT THE  
ANNUAL GENERAL MEETING, 1944.

THE SEVENTY-FIFTH ANNUAL GENERAL MEETING OF THE IRON AND STEEL INSTITUTE was held at the Offices of the Institute, 4 Grosvenor Gardens, London, S.W.1, on Thursday, May 11, 1944, at 10.45 A.M. Mr. JAMES HENDERSON, Retiring President, was in the Chair during the first part of the proceedings, his place being afterwards taken by Mr. ARTHUR DORMAN, the new President.

The Minutes of the previous Meeting were taken as read and signed.

WELCOME TO MEMBERS ATTENDING THE MEETING.

The PRESIDENT (Mr. James Henderson) : This is the seventy-fifth anniversary of the foundation of the Institute, and in other circumstances we should probably have celebrated the occasion in some festive manner; but with the great events now impending this does not seem suitable. We hope that the Institute will long continue to serve its members as well as, and even better than, it has done during the last seventy-five years.

On behalf of the Council, I extend a hearty welcome to all who are here to-day, and especially to representatives of our Allies.

OBITUARY.

The PRESIDENT : The loss of forty members by death is referred to in the Council's Report for 1943. They include two members of the Council, Lord Airedale and Dr. W. H. Hatfield. Lord Airedale joined the Institute as long ago as 1889 and had been an Honorary Vice-President since 1926; he was formerly an active member and a leader among a generation which is now fast passing away. Dr. Hatfield was known to all who came to our meetings, and we shall greatly miss the lively part which he took in our discussions and his enthusiastic guidance of our research activities. I ask you to rise in memory of all the members whom we have lost.

## MEMORIALS TO THE LATE DR. W. H. HATFIELD, F.R.S.

The PRESIDENT : This is an appropriate time to mention that a fund is being raised to found an Annual Memorial Lecture in memory of Dr. Hatfield. The University of Sheffield has agreed to act as trustee. It will be for the Lecture Committee, representing the University, the Royal Society, and this Institute, the three scientific organisations with which Dr. Hatfield was most closely associated, to decide where the Lecture is to be held, but it may well prove a satisfactory arrangement to hold it alternately in Sheffield and in connection with the Annual Meeting of this Institute.

The Joint Research Committees have also taken action to commemorate the services which Dr. Hatfield rendered to research, and I will ask Mr. Dawson, Chairman of the Steel Castings Research Committee, to say something about that.

Mr. W. J. DAWSON (Sheffield) : I am speaking as Chairman of one of the Joint Committees organised by the Institute with which Dr. Hatfield was very closely associated, and also on behalf of Dr. Swinden, the Chairman of the Heterogeneity, Corrosion, and Alloy Steel Committees, who is unfortunately not able to be here. You all know to what an extent Dr. Hatfield devoted his life to the work and inspiration of the various Research Committees, and the members of them, about 170 in all, comprising some twenty-five Joint Committees and Sub-Committees, felt that something ought to be done to commemorate in a suitable manner his connection with them. They decided that perhaps the best form which that could take would be a portrait which could be kept as a memento by The Iron and Steel Institute, and accordingly Mr. James Bateman, R.A., was commissioned to paint this. He has now carried out the work, which is to be seen in the Royal Academy.

It is my duty to ask the President to accept this portrait. I hope that it may be hung on the walls along with others of bygone famous members of the Institute. (*Applause.*)

The PRESIDENT : On behalf of the Council, I thank Mr. Dawson and all the subscribers. Those who were associated with Dr. Hatfield are pleased to think that his connection with the Institute will be perpetuated in this way, and I think the idea is one which would have appealed also to him. The personal affection which we felt for Dr. Hatfield was equal to the devotion which he gave to the welfare of the Institute. The Council propose to hang the portrait in the Library.

## PRESENTATION OF A PICTURE OF THE INSTITUTE.

The PRESIDENT : Mr. R. A. Kirkby has presented to the Institute a fine water-colour of the Institute's building, painted by Mr.

Henry Rushbury, R.A. We are very pleased to have pictures like this which increase the interest and add to the amenities of this house, and the Council thank Mr. Kirkby for his welcome gift.

AWARD OF THE BESSEMER GOLD MEDAL FOR 1944 TO  
MR. ESSINGTON LEWIS, C.H.

The PRESIDENT: You will have been pleased to notice in the Press that the Bessemer Gold Medal for this year has been awarded to Mr. ESSINGTON LEWIS, C.H., Director-General of Munitions and Aircraft Production in Australia, and a member of this Institute since 1921. Mr. Essington Lewis's outstanding services to Australia's war effort were recently acknowledged by the King, when he made him a Companion of Honour. We are happy to be able to pay this tribute to his great services in building up the iron and steel industry in Australia.

BALLOT FOR THE ELECTION OF MEMBERS AND ASSOCIATES.

Dr. DAVID BINNIE (Irlam, near Manchester) and Mr. D. MANTERFIELD (Sheffield), who had been appointed scrutineers of the ballot, reported that the following one hundred and nine candidates for membership and ninety-five for associateship had been duly elected:

MEMBERS.

**Akers**, Ernest Henry (Darlington). **Angus**, Norman Stanley, Assoc. Met. (Sheffield) (Sheffield). **Baillot**, Alfred Gislain, A.M.Inst.B.E. (Leighton Buzzard, Beds.). **Barracough**, Edgar (Norwich). **Beet**, Frederick, B.Met. (Sheffield), (Burnage, Manchester). **Birch**, Raymond E. (Pittsburgh, Pa., U.S.A.). **Bodmer**, Carl Albert, A.M.C.T. (Widnes, Lancs.). **Bowden**, John Stanley, B.Met. (Sheffield) (Hadfield, Manchester). **Braby**, Frederick Cyrus, B.Sc.(Eng.), M.I.Mech.E. (London). **Bridge**, Arthur (Scunthorpe, Lincs.). **Capper**, Hal, B.Sc. (Emsworth, Hants.). **Chalmers**, Bruce, D.Sc., Ph.D., F.Inst.P. (London). **Chisholm**, James (Erdington, Birmingham). **Christiansen**, Herman (London). **Clouston**, George Albert (Redcar, Yorks.). **Clugston**, L. G. (Seawby, Lincs.). **Collinge**, William Chisholm (Bradford). **Corder**, J. A. (London). **Corlett**, William Harold (Hawarden, Chester). **Davis**, Edgar (Twickenham, Middlesex). **Denissenko**, Eugene D. (Washington, D.C., U.S.A.) **Dunn**, James William Robert (Copnor, Hants.). **Ellis**, Geoffrey Courtauld, B.Sc.(Hons. Met.) (Loughborough, Leics.). **Elvish**, Captain Reginald Thomas (Stoke-on-Trent). **Evans**, Richard Arthur Lewis, M.I.E.I. (London). **Fang**, Bin, B.Met. (Sheffield). **Ferguson**, William (Ishapore, India). **Flinn**, Arthur Valentine, A.M.I.Mech.E. (Salford). **Gardner**, Alfred Frederick Charles (Rotherham). **Gravelle**, Richard Charles Hubert (Port Talbot, Glam.). **Gregory**, Clifford H. (Ruislip, Middlesex). **Gregory**, Harold (Sheffield). **Hall**, Norman Reginald, F.R.I.C. (Corby, Northants.). **Hall**, Thomas Henry (London). **Haller**, Percy, M.Sc., F.S.G.T. (Sheffield). **Harrison**, Eric James (Birmingham). **Harrison**, James William (Darlington). **Hawtin**, Albert Sydney (Blackpool). **Hedgecock**, Percy David (London). **Hellman**, Alick, B.Sc.(Eng.) (Vereeniging, Transvaal, South Africa).

Africa). **Hewitt**, Donald Helmsley, M.A.(Cantab.), A.R.I.C. (London). **Hirschler**, Carl (London). **Howgate**, Philip Stephen (Barrow-in-Furness). **Huddle**, Alfred Ulfketel, M.A.(Hons.) (Cantab.) (Cambridge). **Hunter**, Edward (Willenhall, Staffs.). **Iddon**, Robert Alan (London). **Jones**, George (Brymbo, Wrexham). **Keegan**, Cyril Clement, B.E., G.I.Mech.E. (Dublin). **Kemp**, James Taylor, B.Sc. (London). **Kershaw**, Walter (Bolton, Lancs.). **King**, Alan Roy, A.R.C.S., D.I.C. (London). **Kirkland**, John Galloway (Chester). **Kostroun**, Václav, M.Sc.(Prague), A.M.I.Mech.E. (London). **Ladds**, Charles (Scunthorpe, Lincs.). **Langen**, Mathias (Parkstone, Dorset). **Laverton**, William Thomas (Stoke-on-Trent). **Leadbeater**, Cyril James (Teddington, Middlesex). **Legg**, Professor Vernon Howes, F.R.I.C. (Istanbul, Turkey). **Ludlow**, R. (Stourport-on-Severn). **Mannifield**, Joseph Albert (Sheffield). **Mannox**, Frank Cecil (Hornchurch, Essex). **Millington**, Frank (Hawarden, Chester). **Millward**, Edward Bertram (Allenton, Derby). **Morley**, John (Sale, Manchester). **Mukerjee**, Sunil Coomar (London). **Musted**, George Gordon (Sheldon, Birmingham). **Neelands**, Abram Rupert, B.A., M.E., M.I.M.M. (Doncaster). **Nelson**, Philip Henry, G.I.Mech.E. (Middleton, Market Harborough). **Northam**, Flight-Lieut. G. E., A.M.I.Mech.E. (Pinner, Middlesex). **Oxley**, Norman (Cawnpore, India). **Peacock**, John Stephens (Lower Machen, Newport, Mon.). **Prosser**, Cyril Alyster, B.Sc.(Met.) (Wales) (Rumney, Cardiff). **Pryce**, Leonard, Assoc. Met. (Sheffield) (Romiley, Cheshire). **Reilly**, David (Corby, Northants.). **Reynish**, Edgar Reginald (Penylan, Cardiff). **Ridgley**, H. G. (North Wembley, Middlesex). **Roberts**, Benjamin (Sheffield). **Rollin**, Calvert Noble (Glanton, Northumberland). **Roskill**, Oliver Wentworth (London). **Rossz**, Dr. Laszlo, A.M.I.Mech.E. (Kew Gardens, Surrey). **Rowlands**, William Brinley (Redcar, Yorks.). **Samuels**, Richard Frederick, A.R.Ae.S. (Harborne, Birmingham). **Sidwell**, Joseph (Coventry). **Simons**, Eric Norman (Eyam, Sheffield). **Slavin**, Benjamin, B.Met.E. (Sydney, Australia). **Sloman**, Hedley Archibald (Teddington, Middlesex). **Smith**, Frederick Leedham, A.M.I.Mech.E. (Ickenham, Middlesex). **Stead**, Bernard Ashton (Beauchief, Sheffield). **Summers**, Edward Merrett (Melton Mowbray, Leics.). **Symonds**, Hubert Henry (Eastcote, Middlesex). **Thomas**, Henry Cornelius (Birmingham). **Thomas**, Joseph Leslie (Margam, Port Talbot, Glam.). **Thorley**, Thomas, A.M.I.Mech.E., A.M.I.E.E. (Denton, Manchester). **Thring**, Meredith Woolridge, M.A.(Cantab.) (London). **Tricker**, Reginald Ernest Lanham, M.Sc. (Hall Green, Birmingham). **Walters**, William Ivan, M.I.A.E. (Bastead, Surrey). **Waterfall**, Frederick David (Oldbury, Birmingham). **Watkins**, Arthur Edward (Hitchin, Herts.). **Wilkinson**, Major Thomas Basil, R.A., B.Eng., Ph.D., A.M.I.Mech.E. (Swansea). **Willey**, Douglas Holroyd, B.Met.(Hons.) (Sheffield) (Scunthorpe, Lincs.). **Williams**, Sidney George (Cardiff). **Willows**, Richard, M.Sc.(Met.) (Cardiff). **Wilson**, John Leslie (Cawnpore, India). **Winters**, William Thomas M.Inst.W. (Bournbrook, Birmingham). **Wood**, Roger (London). **Worner**, Graham H. (Llasmarl, Swansea). **Wright**, William George (Sydney, Australia). **Zapffe**, Carl Andrew, M.S., Sc.D. (Baltimore, Maryland, U.S.A.). **Zygmans**, Zygmunt (Letchworth, Herts.).

## ASSOCIATES.

**Axon**, Howard James (Sheffield). **Bailey**, Alan Robert (London). **Baulk**, Roland Hugh (London). **Beeley**, Peter Reaney, B.Met. (Crosspool, Sheffield). **Bell**, Gerald Robert (Hornchurch, Essex). **Bolt**,

Norman (Bishopston, Bristol). **Bourne**, Leonard, B.Met. (Sheffield) (Goldthorpe, Rotherham). **Brigg**, John (North Wembley, Middlesex). **Carter**, Alan (Cambridge). **Clegg**, Alan George (Scunthorpe, Lincs.). **Cook**, John Henry (Leeds). **Cope**, Stanley George, B.Sc. (Handsworth, Birmingham). **Davies**, Harold James (Swansea). **Davies**, William Howell (Swansea). **Davis**, Francis Henry (Swansea). **Edwards**, Albert Charles (Smethwick, Staffs.). **Fick**, Nathaniel Crow (Columbus, Ohio, U.S.A.). **Fitzgibbon**, Sergeant John J. (London). **Fletcher**, Stewart Gailey, B.S., Sc.D. (Cambridge, Mass., U.S.A.). **Floyd**, Ronald William, B.Sc.(Hons.) (Lond.) (King's Norton, Birmingham). **Fowler**, Robert Thomas (Swansea). **Garrett**, Fredrick Colin Roy (Thornbury, Bristol). **Gilchrist**, John Kirkland, B.Sc., A.R.T.C. (Sheffield). **Greaves**, William Henry (Bilston, Staffs.). **Grgić**, Slavko (Birmingham). **Griffiths**, Peter Donald (Swansea). **Hall**, Harry Thomas (Radcliffe, Manchester). **Hammond**, Henry Norman (Brightlingsea, Essex). **Hancox**, Donald E. (Radford, Coventry). **Hargreaves**, Fred (London). **Hemsley**, Stephen (Pitsmoor, Sheffield). **Herbert**, David B. (Scunthorpe, Lincs.). **Hobson**, William Edward (Scunthorpe, Lincs.). **Hollomon**, John H. (Newton, Mass., U.S.A.). **Hopkinson**, Cecil Frederick (Scunthorpe, Lincs.). **Hughes**, Thomas Garfield, B.Sc.(Hons.) (Lond.) (Briton Ferry, Glam.). **Hyde**, Philip William, B.Sc. (Bexley Heath, Kent). **James**, Raymond John Charles (Smethwick, Staffs.). **Jenkins**, David Clive (Port Talbot, Glam.). **Johnson**, Arthur Charles William (Loughborough, Leics.). **Jones**, Howell Henry Montagu, B.Sc.(Tech.) (Hons.), G.I.M.E., G.I.Chem.E. (Briton Ferry, Glam.). **Jubb**, Willie (Sheffield). **Kitchiner**, Stuart Gordon (Westoning, Beds.). **Knights**, William John (Northfield, Birmingham). **Ladlow**, A. (Brigg, Lincs.). **Leech**, Edward Arthur (London). **Lindley**, Kenneth (Wrenthorpe, Wakefield). **Little**, Alexander Torrance (Oxford). **Marinca**s, John George (Trenton, N.J., U.S.A.). **Matthews**, Alfred William (Smethwick, Staffs.). **Maycock**, Jack Henry (Erith, Kent). **Mears**, D. A. W. (Stourport-on-Severn). **Miller**, Denzil Kenneth (London). **Milroy**, Alexander Gideon (Feltham, Middlesex). **Monaghan**, John (Wednesbury, Staffs.). **Morgan**, Rees (Port Talbot, Glam.). **Nelmes**, William Stanley (St. Thomas, Swansea). **Noakes**, Francis Donald Lewis (London). **Northwood**, James Edward (Coventry). **Olney**, Maurice Joseph (Swansea). **Osborn**, John Holbrook (Cambridge). **Partridge**, John Montague (Swansea). **Perryman**, Eric Charles William (Farnborough, Hants). **Pidd**, Ralph (Crowle, Scunthorpe, Lincs.). **Pokorny**, Hans Walter (London). **Quinlan**, Joseph (Deepcar, Sheffield). **Rankin**, Alexander Bryce Calder (Motherwell, Lanarkshire). **Reynolds**, Norman Montgomery (Coventry). **Ricks**, Bernard W. (Leicester). **Sanders**, James (Wolverhampton). **Scott**, Francis Hubert (Sheffield). **Scott**, Hubert Dennis (Scunthorpe, Lincs.). **Scott**, William Alexander (Littleover, Derby). **Shipley**, Edward Albert (Coventry). **Smith**, Harold (Crowle, Scunthorpe, Lincs.). **Smith**, Harold Haig (Staines, Middlesex). **Smith**, Hugh (Luton, Beds.). **Stemman**, George T. (Ward End, Birmingham). **Suddaby**, Albert (Stocksbridge, Sheffield). **Summers**, Oliver Rendel (Great Crosby, Liverpool). **Taylor**, George Milne (Silver End, Witham, Essex). **Teanby**, Joseph Donald (Crowle, Scunthorpe, Lincs.). **Thomas**, David John Leighton (Dowlais, Glam.). **Thompson**, Henry James, A.M.I.B.E. (Leighton Buzzard, Beds.). **Walker**, E. Jack (Akron, Ohio, U.S.A.). **Webster**, Charles Allan (Solihull, Birmingham). **Wernick**, Joseph (Penn, Wolverhampton). **Wheeler**, John Alan (Birmingham). **Whiting**, Arthur Noel (Scunthorpe,

Lines.). **Wilkinson**, Frederick Lawrence (Accrington, Lancs.). **Williams**, Jack (Cardiff). **Willsher**, William Leslie (Scunthorpe, Lines.). **Wilson**, Francis Stowell (Cambridge). **Wood**, Kenneth Gordon (Penistone, Sheffield). **Young**, John Stewart (Airdrie, Lanarkshire).

#### ELECTION OF VICE-PRESIDENTS AND MEMBERS OF COUNCIL.

The SECRETARY (Mr. K. Headlam-Morley) : In accordance with Bye-law 10 the names of the following Vice-Presidents and Members of Council were announced at the Autumn Meeting, 1943, as being due to retire at the present Annual Meeting :

*Vice-Presidents* : Dr. W. H. Hatfield, F.R.S., Sir William Larke, K.B.E., and Mr. C. E. Lloyd, M.P.

*Members of Council* : Dr. C. A. Edwards, F.R.S., Mr. G. H. Latham, Mr. E. F. Law, Mr. R. Mather and Sir Arthur B. Winder, J.P.

Owing to the death of Dr. Hatfield, Vice-President, Dr. A. McCance, F.R.S., became due to retire in his stead.

No other members having been nominated up to one month previous to the present meeting, the retiring Vice-Presidents and Members of Council are now presented for re-election. (*Agreed.*)

#### PRESENTATION OF REPORT OF COUNCIL AND STATEMENT OF ACCOUNTS FOR 1943.

The PRESIDENT presented the Report of Council for 1943 (*see pp. 14 p-33 p*). He pointed out that the membership at the end of the year, namely, 2800, which did not include some 300 members whose names were on suspense lists, was the highest yet reached. It was particularly encouraging that the number of Associates had increased during the year by 25%.

The Hon. R. G. LYTTELTON (Honorary Treasurer) presented the Statement of Accounts for 1943 (*see pp. 34 p-41 p*). In reviewing the principal features he said : It is apparent that the satisfactory condition of our financial position is to a great extent due to the Special Subscriptions from Companies, which have amounted on an average during the last five years to just under £4500 per annum. It was the original intention of the Council, when they asked the industry to give these subscriptions, that the money should be devoted to removing financial anxiety for a period of seven years and enabling the Institute to continue to finance research and other services for the industry and the members, the view being that during that time our activities would increase, our Membership would be built up and our financial position would be such that the normal income would exceed the expenditure. This period has been interrupted by the war for at least five years, and, although we have

made considerable progress, many things have had to be postponed. The additional expenditure and loss of income occasioned by the war amount to at least £3000 a year.

Taking these considerations into account, and in view of the increased expenditure to be faced after the war, the Council have decided to invite companies to continue their subscriptions for a few years longer than had been originally anticipated. I would finish by saying how much the Council appreciate the very generous subscriptions that have been given by the industry.

The PRESIDENT's motion that the Report of Council and Statement of Accounts for 1943 be adopted was carried unanimously.

#### THE BRITISH IRON AND STEEL RESEARCH ASSOCIATION.

The PRESIDENT : Two years ago, in my Presidential Address, I referred to the need for intensifying the industry's research activities. You will have seen from the Press, and I am pleased to confirm, that the British Iron and Steel Research Association has recently been formed for this purpose. Members of the Association will be companies who are members of the British Iron and Steel Federation and its allied associations, while associate membership of connected industries is provided for. The Federation will nominate 22 members of the Council and the Institute 9; there is, therefore, proper recognition of the important part which the Institute has played since its inception in fostering technical and scientific development, and notably during the last twenty years through the Joint Research Committees. We wish every success to the new Research Association. Those responsible for its guidance know that any move to further the prosperity and wellbeing of our industry can count in the future, as always in the past, on the heartfelt support and assistance of this Institute.

#### THE SUPPLY AND STATUS OF METALLURGISTS—NATIONAL CERTIFICATES IN METALLURGY.

The PRESIDENT : Considerable thought has been given by your Council and by the Committee appointed by them to questions affecting the future status and wellbeing of metallurgists. We wish to pay tribute to the foresight of the Advisory Council of the Department of Scientific and Industrial Research in appointing a Committee, of which Dr. McCance is Chairman, to investigate the supply of metallurgists after the war, and we are looking forward to seeing their report. The Council submitted a report to that Committee and gave evidence, and, arising out of these investigations, authorised the publication of a paper on "The Training of Metallurgists,"<sup>1</sup> which has attracted a good deal of attention.

<sup>1</sup> See pp. 601 p–631 p of this Journal.

Jointly with the Institution of Mining and Metallurgy and the Institute of Metals, the Council have agreed to sponsor National Certificates in Metallurgy. These will be operated by a Committee of the three Metallurgical Institutes and the Board of Education, and we hope that they will prove a real encouragement to the many lads who attend part-time courses in technical colleges. An announcement will be made soon.

I think it is an open secret that, together with the Institute of Metals, we are studying the possibility of assisting metallurgists to attain professional status equal to that enjoyed, with such great benefit, by engineers, chemists and members of other professions.

These matters will all play their part in improving the technical education and professional status of the scientists and technicians in our industry. They form a complement to the improvement of technical education which should result from the Bill now before Parliament.

#### COLLABORATION WITH THE INSTITUTE OF METALS.

The PRESIDENT : You will have gathered that in these several matters of considerable importance we have been working very closely with the Institute of Metals. We are happy that this should be the case. Over 800 individuals are members of both Institutes, and the arrangement by which we have shared this building and our libraries has worked well over a number of years. It would appear to be in the best interests of both Institutes to strengthen this association. I am therefore particularly pleased that it fell to me, as your President, to suggest that the Presidents of the Institute of Metals should become Honorary Members of our Council during their terms of office. That invitation was accepted, and a cordial suggestion made that the arrangement should be reciprocal. It is for this reason that we welcome Dr. W. T. Griffiths here to-day, not only as President of the Institute of Metals but also as an Honorary Member of our Council; and I am very pleased that my friend Sir John Greenly, who has done so much to bring the two Institutes closer together, accepted a personal invitation, on retiring from the Presidency of the Institute of Metals recently, to become one of our Honorary Vice-Presidents.

At the request of the Council of the Institute of Metals, we have agreed that our Secretary, Mr. Headlam-Morley, should be appointed to act also as Secretary of that Institute on the retirement of their present Secretary, Mr. Shaw Scott, at the end of June. The arrangement will be in the first instance for a period of one year. We agree with the Council of the Institute of Metals that it is well worth exploring the possibility of the two Institutes working still more closely together, as will no doubt result if we have the same Secretary.

## INDUCTION OF THE PRESIDENT-ELECT, MR. ARTHUR DORMAN.

Mr. JAMES HENDERSON (Retiring President) : I now come to the end of my office by asking you to receive Mr. Arthur Dorman as your President. As our time is precious, I shall not say much about him—and the name of Dorman is almost enough. Messrs. Dorman Long & Co., Ltd., are known throughout the world both for plain material and for fabricated, and, as Australia is much in the news nowadays, I need only say that Sydney Bridge is an example of their work. Mr. Dorman's own career has been completely identified with his company, except for the period of the last war, when he served with the Green Howards. Besides being an Executive Director of Dorman Long, he is Chairman of several of their associated companies, and has held in past years the Presidency of the British Iron and Steel Federation, the National Federation of Employers' Organisations, the Cleveland Institute of Engineers and others. He brings to his new office the widest knowledge of our industry and a very full experience of administrative work. I know that you will accord him the sympathetic support which you have always given me. (*Applause.*)

Mr. HENDERSON then left the Chair, which was taken, amid applause, by the incoming President, Mr. ARTHUR DORMAN.

NOMINATION OF MR. JAMES HENDERSON TO BE AN  
HONORARY MEMBER.

The PRESIDENT (Mr. Arthur Dorman) : I feel highly honoured to be installed in this Chair to-day. My first duty, and a very pleasant one, is to propose a vote of thanks to Mr. James Henderson. The two years for which he has been President have been two vital years. He has very wisely reviewed the activities of the Institute in connection with research and other matters of importance to us, and we know that his own activities in that connection have been of great value both to the Institute and to the trade.

Mr. Henderson is a very old friend of my own ; I have known him for at least 26 years, and possibly a few more. He is chiefly identified with the Frodingham district, where he has done wonderful work, although he was born in Glasgow. I have been with him on some of the commercial associations, where he was a dour fighter. I remember him as President of the Federation when we had our first cartel discussions.

Mr. Henderson has been a member of this Institute for 52 years (*applause*), and the Council this morning, with real sincerity and unanimity, elected him an Honorary Member of the Institute. (*Applause.*) By your applause you have shown that you endorse that decision with enthusiasm. No one deserves this honour more than he does, after giving his life to our industry.

*Complete List of Papers and Report Presented at the Annual General Meeting, 1944.*

- BLAST-FURNACE MATERIALS ANALYSIS SUB-COMMITTEE OF THE BLAST-FURNACE COMMITTEE : "The Determination of Sulphur and Phosphorus in Pig Iron."
- D. BINNIE : "A Study of a Shell-Steel Ingot. (Paper No. 25/1943 of the Committee on the Heterogeneity of Steel Ingots).
- N. L. EVANS : "The Use of Basic-Lined Ladles in the Desulphurisation of Cast Iron by Sodium Carbonate."
- N. L. EVANS : "Cleaning and Descaling Steel by Electrolytic Pickling in Molten Caustic Soda."
- R. W. EVANS : "The Heating of Open-Hearth Furnaces with Mixed Coke-Oven and Blast-Furnace Gas."
- U. R. EVANS : "Progress in the Corrosion Research Section at Cambridge University." (Paper No. 12/1943 of the Corrosion Committee).
- J. A. HALL : "The Drift of Selenium Photo-Electric Cells in Relation to their Use in Temperature Measurement." (Paper No. 26/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Liquid Steel Temperature Sub-Committee)).
- K. HOSELITZ : "The Iron-Nickel Phase Diagram by Magnetic Analysis and the Effects of Cold-Work."
- A. W. HOTHERSALL, D. W. HOPKINS and G. L. EVANS : "Factors Affecting the Strength of Soldered Joints made from Electro-Tinned Steel Sheet."
- A. U. HUDDLE and U. R. EVANS : "Some Measurements of Corrosion-Fatigue made with a New Feeding Arrangement." (Paper No. 11/1943 of the Corrosion Committee).
- J. E. HURST and R. V. RILEY : "A Note on the Microstructure of High-Silicon Acid-Resisting Iron."
- J. E. HURST and R. V. RILEY : "The Occurrence of the Carbide Phase in High-Silicon Iron-Carbon Alloys."
- A. JACKSON : "Some Notes on Slags and Slag Control in Basic Open-Hearth Tilting Furnaces using Phosphoric Iron."
- T. LAND : "Barrier-Layer Photo-Electric Cells for Temperature Measurement." (Paper No. 6/1943 of the Steel Castings Research Committee (submitted by the Foundry Steel Temperature Sub-Committee)).
- A. H. LECKIE : "The Study of the Thermal Performance of Open-Hearth Furnaces by the Correlation of Operating Data."
- H. LIPSON and AUDREY M. B. PARKER : "The Structure of Martensite."
- D. MANTERFIELD : "Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces." (Paper No. 23/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Liquid Steel Temperature Sub-Committee)).
- D. A. OLIVER and T. LAND : "A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures." (Paper No. 5/1943 of the Steel Castings Research Committee (submitted by the Foundry Steel Temperature Sub-Committee)).
- N. J. PETCH : "The Interpretation of the Crystal Structure of Cementite."
- A. PREECE and R. V. RILEY : "The Scaling Properties of Steels in Furnace Atmospheres at 1150° C." (Paper No. 14/1943 of the Alloy Steels Research Committee).
- D. J. PRICE and H. LOWERY : "The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red." (Paper No. 7/1943 of the Steel Castings Research Committee (submitted by the Foundry Steel Temperature Sub-Committee)).

- T. H. SCHOFIELD : "Note on some Unusual Microstructures Observed in Mild and Medium-Carbon Steels."
- W. STEVEN : "The Effect on the Hardenability of Small Additions of Chromium and Molybdenum to a Grain-Size-Controlled 0·9% Nickel Steel."
- T. SWINDEN : "The Examination of a Rimming-Steel Ingot containing 0·29% of Carbon." (Paper No. 27/1944 of the Committee on the Heterogeneity of Steel Ingots).
- T. SWINDEN, W. W. STEVENSON and G. E. SPEIGHT : "Rimming Steel.—An Examination of the Carbon and Oxygen Relationship in the Solidification of Basic Open-Hearth Steel." (Paper No. 24/1943 of the Committee on the Heterogeneity of Steel Ingots).
- T. SWINDEN, W. W. STEVENSON and G. E. SPEIGHT : "Rimming Steel.—Experiments on Melts of Rimming-Steel Composition in the Laboratory High-Frequency Furnace." (Paper No. 28/1944 of the Committee on the Heterogeneity of Steel Ingots).
- W. J. WRAZEJ : "The Apparent Microstructure Produced by Hydrofluoric Acid Etching Reagents on Pure Iron and Iron-Silicon Alloys."
- "Review of the Work of the Joint Research Committees, 1924–1943, of The Iron and Steel Institute and The British Iron and Steel Federation reporting to the Iron and Steel Industrial Research Council." (The Iron and Steel Institute, 1943, Special Report No. 29).
- "The Training of Metallurgists, with Special Reference to the Iron and Steel Industries." Issued by authority of the Council of The Iron and Steel Institute.

Professor THOMAS TURNER (Leatherhead) : It is with very great pleasure that I second the vote of thanks. The President said he had known Mr. Henderson for 26 years, but I have had the pleasure of knowing him for 50. The younger generation of members will know more about what he has done for the Institute recently. Not only did he act as a Member of Council for a long time, but he was our trusted Honorary Treasurer for a number of years before becoming President. During his term of office he has had some most difficult questions to consider, and he has dealt with them with care, and I would almost say with enthusiasm.

The vote of thanks was carried unanimously, with acclamation.

Mr. JAMES HENDERSON : I am quite overcome by the honour which you have accorded me, and by the enthusiasm with which it has been greeted. I can only say, as one well on in a longish life, that nothing could have given me greater pleasure than to feel that what I have been able to do for the industry, and particularly for the Institute, has been appreciated. I thank you very much.

#### SERVICES OF THE STAFF.

Mr. HENDERSON (*continuing*) : On giving up my office, I want to thank all the members of the staff for their loyal service under very great difficulties—shortage of numbers, the blackout and so on. Their services have been rendered with great loyalty, zeal and goodwill. Mr. Chattin, as Assistant Secretary, has done

yeoman service. I wish particularly to mention our Librarian, Mr. Elsdon, who completes forty years' service this year, and to pay a well-deserved tribute to the admirable way in which he has built up our Library from small beginnings until now, as the Joint Library of the two Institutes, it performs a very real service to the members of both the iron and steel and the non-ferrous metals industries. Miss Davison, his assistant, has recently completed 25 years' service, and we congratulate her. Miss Dowd, our accountant, also completed 25 years' service early this year, but I am sorry to say that she is now seriously ill; we hope to see her back again soon.

I cannot close without saying a word about our Secretary, Mr. Headlam-Morley, who came to us just ten years ago, young and untried in this class of work. He threw himself whole-heartedly into it. Especially near to his heart is the work of the Joint Research Committees, to whose members I do not need to commend him. It is interesting to note that during his term of office the total membership of the Institute has increased by 50%, and, what is specially significant, the British membership has been doubled. I thank him for all the help he has given me during my Presidency.

#### PRESENTATION OF THE PRESIDENTIAL ADDRESS.

The PRESIDENT (Mr. Arthur Dorman) then delivered his Presidential Address. The text will be found on pp. 42 P-48 P.

Sir WILLIAM LARKE, K.B.E. (Vice-President) : It falls to me to have the privilege of expressing our thanks to our President for his interesting Address. I feel that a Presidential Address should reflect just sufficiently on the past to give us the benefit of its lessons in dealing with the present and to indicate the path which we should follow in the future. It will be agreed that Mr. Dorman's Address complies with every article in that specification; it is worthy of the name he bears, and we congratulate him upon it and ourselves on the privilege of having it addressed to us.

#### PRESENTATION OF PAPERS.

A list of all the papers included in the programme of the Meeting will be found on pp. 10 P.-11 P. The following were presented for verbal discussion :

##### *Morning Session.*

- “The Heating of Open-Hearth Furnaces with Mixed Coke-Oven and Blast-Furnace Gas.” By R. W. EVANS.
- “The Study of the Thermal Performance of Open-Hearth Furnaces by the Correlation of Operating Data.” By A. H. LECKIE.

The above papers were discussed jointly.

*Afternoon Session.*

- "Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces." By D. MANTERFIELD. (Paper No. 23/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Liquid Steel Temperature Sub-Committee)).
- "Barrier-Layer Photo-Electric Cells for Temperature Measurement." By T. LAND. (Paper No. 6/1943 of the Steel Castings Research Committee (submitted by the Foundry Steel Temperature Sub-Committee)).
- "A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures." By D. A. OLIVER and T. LAND. (Paper No. 5/1943 of the Steel Castings Research Committee (submitted by the Foundry Steel Temperature Sub-Committee)).
- "The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red." By D. J. PRICE and H. LOWERY. (Paper No. 7/1943 of the Steel Castings Research Committee (submitted by the Foundry Steel Temperature Sub-Committee)).
- "The Drift of Selenium Photo-Electric Cells in Relation to their Use in Temperature Measurement." By J. A. HALL. (Paper No. 26/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Liquid Steel Temperature Sub-Committee)).

The above papers were discussed jointly.

- "A Study of a Shell-Steel Ingot." By D. BINNIE. (Paper No. 25/1943 of the Committee on the Heterogeneity of Steel Ingots).
- "The Examination of a Rimming-Steel Ingot containing 0·29% of Carbon." By T. SWINDEN. (Paper No. 27/1944 of the Committee on the Heterogeneity of Steel Ingots).

The above papers were discussed jointly.

## REPORT OF COUNCIL FOR 1943.

THE Council submit this, their Annual Report and Statement of Accounts for the year 1943 to Members for their approval at the Seventy-Fifth Annual General Meeting of The Iron and Steel Institute. Information up to 31st March, 1944, has been included in some sections of the Report.

The facilities provided by the Institute for its Members and the iron and steel industries have been maintained, and increased use has been made of them. Participation in the industry's co-operative research activities has been actively continued.

### ROLL OF THE INSTITUTE.

Membership at the end of the year totalled 2800 and was greater than on any previous occasion. The total number of Members increased by 8% during the year, those resident in Great Britain by 7% and Associates by 25%. Eight hundred and seven Members and Associates, or over 28% (compared with 27% at the end of the previous year), were Members also of the Institute of Metals. Particulars are given in Tables I. and II. and in Fig. 1.

The current Roll of Members does not include those who have been placed on suspense lists. These at 31st December, 1943, consisted of 49 Members and Associates absent on military service, &c., and 247 Members and Associates resident in occupied territory or in neutral countries on the Continent.

*TABLE I.—Membership at 31st December, 1943, and Preceding Four Years.*

	31/12/'39.	31/12/'40.	31/12/'41. <sup>1</sup>	31/12/'42.	31/12/'43.
Patron . . . .	1	1	1	1	1
Honorary Members . .	15	14	15	14	12
Life Members . .	68	67	60	60	64
Ordinary Members : <sup>2</sup>					
Home . . . .	1622	1673	1698	1753	1883
Overseas . . . .	785	663	515	460	471
Associates . . . .	213	248	262	295	369
Total . . . .	2704	2666	2551	2583	2800

<sup>1</sup> Revised.      <sup>2</sup> The above figures include six Members for 1942, seven for 1943 and eight for the other years whose names were retained in the List of Members in an honorary capacity by order of the Council.

Forty deaths were reported during the year and 59 Members and 6 Associates resigned. Two hundred and eighteen Members and 117 Associates were newly elected or reinstated.

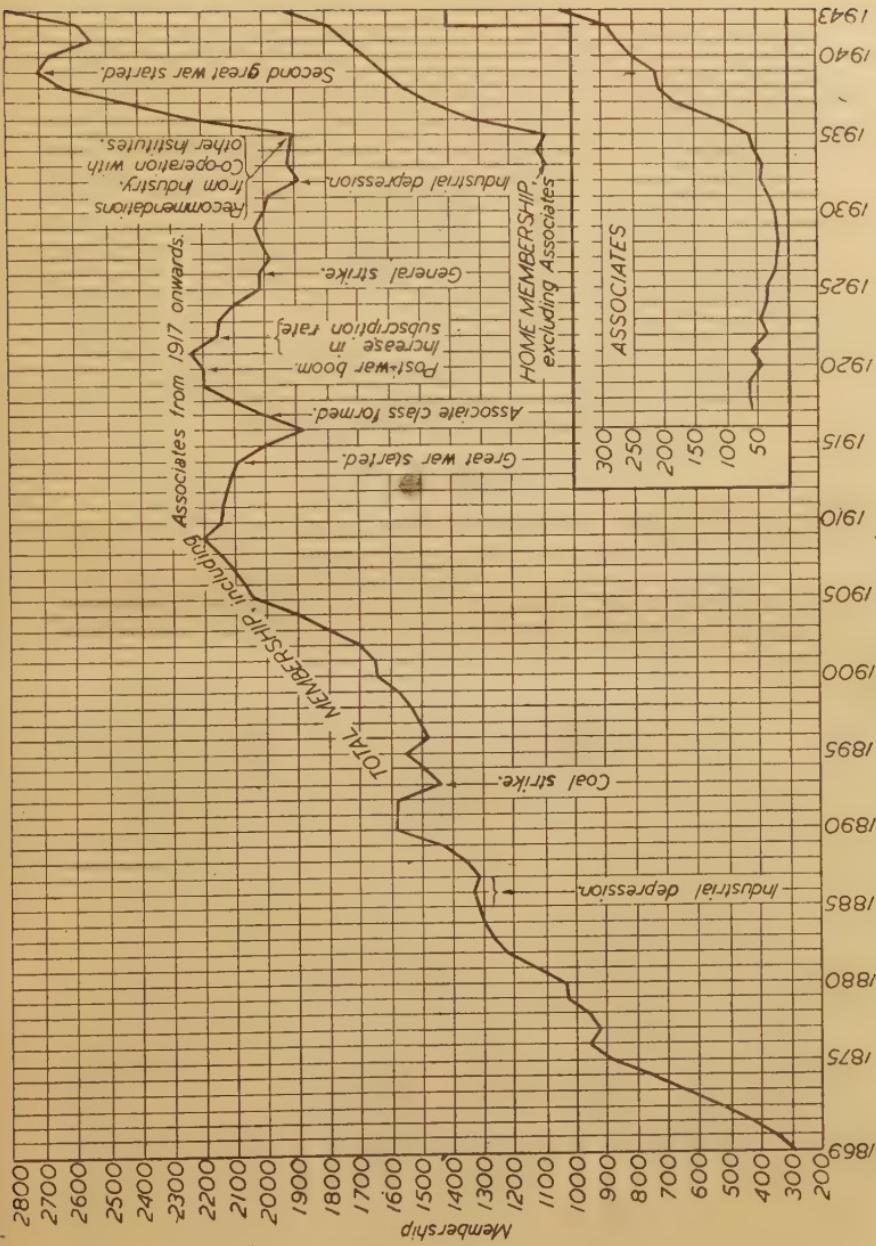


FIG. 1.—Variation in Membership since the Foundation of the Institute in 1869.

TABLE II.—*Composition of Membership at 31st December, 1943.*

	Home Members.		Overseas Members.		Total.	
	Ordinary.	Joint. <sup>1</sup>	Ordinary.	Joint. <sup>1</sup>	Ordinary.	Joint. <sup>1</sup>
Patron . . .	1	...	...	...	1	...
Honorary Members . . .	3	2	6	1	9	3
Life Members . . .	37	6	17	4	54	10
Ordinary Members . . .	1426 <sup>2</sup>	457	342	129	1768	586
Total (Members) . . .	1467	465	365	134	1832	599
Associates . . .	144	188	17	20	161	208
Total (classified) . . .	1611	653	382	154	1993	807
<b>Total Membership</b> . . .					<b>2800</b>	

<sup>1</sup> Members who are also Members of the Institute of Metals.

<sup>2</sup> Includes seven Members whose names were retained in the List of Members in an honorary capacity by order of the Council.

### OBITUARY

The Council regret to record the deaths of the following thirty-four Members which occurred during the year 1943 :

ATERMAN, M. (Corby) . . . . .	22nd February.
ATKINSON, J. S. (East Moseley) . . . . .	18th September.
BAGLEY, C. J. (Hartburn) ( <i>Hon. Vice-President</i> ) . . . . .	1st March.
BARRASS, W. (Sheffield) . . . . .	23rd May.
BOSTOCK, F. J. (Stalybridge) . . . . .	10th November.
BRADFORD, L. (Newcastle, Australia) . . . . .	22nd June.
BURTON, T. G. H. (East Grinstead) . . . . .	30th March.
BUTLER, H. M. (Leeds) . . . . .	10th October.
CALOW, T. A. (Sheffield) . . . . .	9th February.
CLARK, H. (Scunthorpe) . . . . .	January.
CLAXTON, C. W. (Sheffield) . . . . .	19th October.
DIGBY, W. P. (London) . . . . .	5th July.
DYSON, W. H. (Reading) . . . . .	May.
FARRELL, J. A. (New York, U.S.A.) ( <i>Hon. Vice-President</i> ) . . . . .	29th March.
HABERSHON, A. R. (Rotherham) . . . . .	6th December.
HATFIELD, Dr. W. H., F.R.S. (Sheffield) ( <i>Vice-President</i> ) . . . . .	17th October.
HILTON, Sir ROBERT S. (Shipston-on-Stour, Warwickshire) ( <i>Vice-President</i> ) . . . . .	10th October.
JONES, J. J. A. (Sheffield) . . . . .	1st November.
KENNEY, E. F. (Bethlehem, Pa., U.S.A.) . . . . .	8th July.
KING, CARL (Palma, Mass., U.S.A.) . . . . .	25th June.
LORD, F. A. B. (London) . . . . .	19th January.

OWEN, W. P. (Copnor, Portsmouth)	.	.	30th September.
PATON, JOHN (Pontypool)	.	.	18th February.
RAWLIN, E. R. (Rotherham)	.	.	11th January.
READ, Professor A. A. (Bournemouth)	.	.	25th September.
RIDGE, H. M. (London)	.	.	4th August.
ROBINSON, N. (Leamington Spa)	.	.	April.
RUSSELL, F. S. (Cheltenham)	.	.	8th September.
SANDERS, T. H. (Leeds)	.	.	2nd January.
SMITH, F. G. (London)	.	.	1st March.
TOUCEDA, Professor E. (New York)	.	.	20th October.
VOGEL, J. L. F. (Widnes, Lancs.)	.	.	30th August.
WOODWARD, R. G. (Sheffield)	.	.	27th August.
WOOLDRIDGE, W. J. Pittsburgh, Pa., U.S.A.)			6th May.

The deaths of the following six Members took place earlier than 1943, but were not previously reported :

BEAUMONT-THOMAS, Lieut.-Col. L., M.C., (Madley, Hereford)	.	.	December, 1942.
Lieut.-Col. Beaumont-Thomas was reported missing in December, 1942, and in May, 1943, officially reported killed in action.			
BELBIN, H. L. (Sheffield)	.	.	October, 1942.
CHIVERS, F. H. (Llanelli)	.	.	10th July 1942.
LACEY, M. J. (Sydney, Australia)	.	.	November, 1942.
LEWIS, G. J. (Swansea)	.	.	31st August, 1942.
WEST, A. (Glasgow)	.	.	24th April, 1942.

Mr. C. J. Bagley and Mr. James A. Farrell were Honorary Vice-Presidents and Dr. W. H. Hatfield, F.R.S., and Sir Robert S. Hilton, Vice-Presidents. Obituary notices will be found in the No. II. volume of the *Journal* for the year 1943.

Since the end of the year the Council have learned with regret of the death of The Right Hon. Lord Airedale of Gledhow on 11th March, 1944, an Honorary Vice-President and a member since 1889.

### FINANCE.

(*The Statement of Accounts for 1943 is attached to this Report.*)

*General Fund Balance Sheet.*—The Balance Sheet is presented in the usual form. A general reserve was formed by the allocation of £500 and substantial additions were made to existing suspense and reserve accounts.

*General Fund Income and Expenditure Account.*—Income was 7% and expenditure under 2% higher than in the previous year. Receipts from subscriptions and sales of publications are believed to be higher than on any previous occasion.

*Trust Funds.*—The financial position of the Trust Funds was well maintained.

*Investments.*—The value of the investments of the General and

Trust Funds at the end of the year was £74,305, or £8007 in excess of their cost, at which they are taken into the Balance Sheets.

*House Fund and Industrial Subscriptions.*—Income from special subscriptions was £4414. The Council acknowledge with thanks receipt of a new subscription from Gillette Industries, Ltd., and wish to take this opportunity of again expressing their thanks to the following subscribers : Edgar Allen & Co., Ltd.; Ashmore, Benson, Pease & Co., Ltd.; Babcock and Wilcox, Ltd.; Bairds and Scottish Steel, Ltd.; Baldwins, Ltd.; Arthur Balfour & Co., Ltd.; Frederick Braby & Co., Ltd.; Bradley and Foster, Ltd.; The Briton Ferry Steel Co., Ltd.; Burnell & Co., Ltd.; The Butterley Co., Ltd.; Bynea Steel Works, Ltd.; Colvilles, Ltd.; Consett Iron Co., Ltd.; The Darlington Forge, Ltd.; The Darwen and Mostyn Iron Co., Ltd.; Darwins, Ltd.; Dorman, Long & Co., Ltd.; English Steel Corporation, Ltd.; Thos. Firth and John Brown, Ltd.; General Refractories, Ltd.; Guest Keen Baldwins Iron and Steel Co., Ltd.; J. J. Habershon & Sons, Ltd.; Hadfields, Ltd.; N. Hingley & Sons, Ltd.; William Jessop & Sons, Ltd.; Kayser, Ellison & Co., Ltd.; The Lancashire Steel Corporation, Ltd.; Arthur Lee & Sons, Ltd.; The Llanelli Steel Co. (1907), Ltd.; John Lysaght, Ltd.; McCall & Co. (Sheffield), Ltd.; The Millom and Askam Hematite Iron Co., Ltd.; The Mond Nickel Co., Ltd.; Neepsend Steel and Tool Corporation, Ltd.; Newton Chambers & Co., Ltd.; The Oughtibridge Silica Firebrick Co., Ltd.; The Park Gate Iron and Steel Co., Ltd.; The Patent Shaft and Axletree Co., Ltd.; Raine & Co., Ltd.; Round Oak Steel Works, Ltd.; Simon-Carves, Ltd.; Walter Somers, Ltd.; The South African Iron and Steel Industrial Corporation, Ltd.; South Durham Steel and Iron Co., Ltd.; South Wales Siemens Steel Association; The Stanton Ironworks Co., Ltd.; The Steetley Lime and Basic Co., Ltd.; John G. Stein & Co., Ltd.; Stewarts and Lloyds, Ltd.; John Summers & Sons, Ltd.; Tata, Ltd.; Taylor Bros. & Co., Ltd.; Richard Thomas & Co., Ltd.; The Tinsley Rolling Mills Co., Ltd.; The Union Steel Corporation (of South Africa), Ltd.; The United Steel Companies, Ltd.; The Upper Forest and Worcester Steel and Tinplate Works, Ltd.; Vickers, Ltd.; The Wellman Smith Owen Engineering Corporation, Ltd.; The Welsh Plate and Sheet Manufacturers' Association; Whitehead Iron and Steel Co., Ltd.; The Woodall-Duckham Vertical Retort and Oven Construction Co. (1920), Ltd.

The Council wish also to record their thanks to The Kennedy Press, Ltd., from whom a subscription for five years has been received since the end of the year.

#### LEGACY BY THE LATE SIR ROBERT HADFIELD, Bt., F.R.S.

A legacy of £250 was left to the Institute by the late Sir Robert Hadfield, Bt., F.R.S., Past-President, to found a prize in connection with the alloys of iron and steel or to be used for such purpose as

the Council think best. The Council have decided to defer a decision as to the best use to be made of this legacy until after the war and have ordered the proceeds to be invested.

#### CHANGES ON THE COUNCIL.

(To 31st March, 1944.)

The President announced at the Autumn Meeting that Mr. Arthur Dorman had been unanimously nominated to succeed him at the Annual Meeting in 1944.

During the year Mr. W. J. Brooke, J.P., was nominated an Honorary Vice-President, and Mr. P. B. Brown and Captain H. Leighton Davies, C.B.E., Vice-Presidents. Mr. W. B. Baxter (Appleby-Frodingham Steel Co., Ltd.), Mr. W. J. Dawson (Messrs. Hadfields, Ltd.) and Mr. D. R. Lysaght (Messrs. John Lysaght, Ltd.) were elected Members of Council. Mr. R. Staton, Mr. F. Wardrobe, Mr. B. Thomas and Provost J. Tennent accepted invitations to become Honorary Members of Council during their presidencies of the Sheffield Metallurgical Association, the Sheffield Society of Engineers and Metallurgists, the Staffordshire Iron and Steel Institute and the West of Scotland Iron and Steel Institute in succession to Mr. G. Glenn, the late Dr. W. H. Hatfield, F.R.S., Mr. A. Wright and Colonel Alan Stein, M.C., T.D., D.L., respectively.

In December, 1943, Lieut.-Col. Sir John Greenly, K.C.M.G., became an Honorary Member of Council in accordance with the arrangements made with the Institute of Metals by which the President of each Institute was to serve as an Honorary Member of Council of the other. He was succeeded by Dr. W. T. Griffiths on relinquishing the Presidency on 15th March, 1944. Sir John Greenly then accepted an invitation to become an Honorary Vice-President.

In accordance with Bye-Law No. 10, the names of Vice-Presidents and Members of Council due to retire at the Annual Meeting in 1944 were announced at the Autumn Meeting, 1943. Owing to the death of Dr. W. H. Hatfield, F.R.S., Dr. A. McCance, F.R.S., is due to retire in his stead, and the list of those retiring is accordingly as follows :

*Vice-Presidents.*—Sir William Larke, K.B.E., Mr. C. E. Lloyd, M.P., and Dr. A. McCance, F.R.S.

*Members of Council.*—Principal C. A. Edwards, F.R.S., Mr. G. H. Latham, Mr. E. F. Law, Mr. R. Mather, Sir Arthur Winder and Mr. N. H. Rollason.

No other members having been nominated up to one month previous to the Annual Meeting, the retiring members are presented for re-election.

**BESSEMER GOLD MEDAL.**

The Bessemer Gold Medal for 1943 was awarded to Mr. John Hampden Whiteley, of the Consett Iron Co., Ltd., in recognition of his numerous and valuable contributions to knowledge of the metallurgy and metallography of iron and steel, with special reference to his study of the acid hearth and slag and his examination of the nature of inclusions in steel.

The Bessemer Gold Medal for 1944 has been awarded to Mr. Essington Lewis, C.H., Director-General of Munitions and Aircraft Production, Australia, in recognition of his outstanding services to the iron and steel industry of Australia.

**ANDREW CARNEGIE MEDAL.**

No award of the Andrew Carnegie Medal was made during the year.

**WILLIAMS PRIZE.**

A Williams Prize (1942) of £100 was awarded to Mr. A. Jackson, of the Appleby-Frodingham Steel Co., Ltd., for his paper on "The Linings of Large Basic Open-Hearth Tilting Furnaces," printed in the No. II. *Journal* for 1942.

In addition, a Williams Prize (1943) of £100 was awarded to Mr. R. L. Knight, of Australian Iron and Steel, Ltd., for his paper entitled "A Review of Basic Open-Hearth Practice at an Australian Plant," which will be found in the No. I. volume of the *Journal* for 1943.

**ANDREW CARNEGIE RESEARCH SCHOLARSHIP.**

A grant was made by the Council in 1943 to :

M. S. WANG (Sheffield University)—£150 in aid of an investigation on the effect of repeated heat treatment on steels.

**THE WORSHIPFUL COMPANY OF BLACKSMITHS.**

No recommendation for admission to the Worshipful Company of Blacksmiths was made during the year.

**HONOURS CONFERRED ON MEMBERS.**

(*To 31st March, 1944*).

The Council tender their warmest congratulations to the following Members of the Institute for honours and appointments received during the period under review :

ANDREW, Professor J. H.—Elected a Member of Council of the Institute of Metals.

BAKER, GEORGE.—Elected President of the Sheffield and District Engineering Trades Employers' Association.

- BALLARD, W. E.—Granted the Fellowship of the Royal Institute of Chemistry.
- BRUCE-GARDNER, Sir CHARLES.—Appointed Controller of Labour Allocation and Supply in the Ministry of Aircraft Production; will be a member of the Aircraft Supply Council.
- COTTAM, H. D.—Appointed a Justice of the Peace for Rotherham.
- CRAIG, JOHN.—Created a Knight Bachelor.
- DE SCH, Dr. C. H., F.R.S.—Awarded the honorary degree of LL.D. of Glasgow University.
- DUDLEY, The Rt. Hon. the Earl of, M.C.—Elected President of the Federation of Chambers of Commerce of the British Empire.
- EDWARDS, T. W.—Appointed a Justice of the Peace for Rotherham.
- ELLIOT, I. F. L.—Appointed Chairman of the Eastern Group Supply Council.
- GOUGH, F. H. B.—Created an Officer of the Order of the British Empire.
- GOUGH, Dr. H. J., C.B., M.B.E., F.R.S.—Designated Director-General of Scientific Research and Development to the Ministry of Supply (instead of Director of Research).
- GREGORY, Dr. E.—Appointed Assistant Director in charge of Metallic Materials, Aeronautical Inspection Directorate, Ministry of Aircraft Production.
- GRIFFITHS, Dr. W. T.—Elected President of the Institute of Metals for 1944–45.
- GROSSMANN, Dr. M. A.—Elected President of the American Society for Metals.
- HOLLINGS, J. S.—Created a Commander of the Order of the British Empire.
- JEFFRIES, Dr. ZAY.—Awarded the Gold Medal of the American Society for Metals.
- KILBY, J. N.—Elected Chairman of the Lincolnshire Iron-masters' Association for the second year in succession. Elected President of the Lincolnshire Iron and Steel Institute for 1943.
- LAYCOCK, COLIN.—Elected President of the Sheffield Chamber of Commerce.
- LEA, Dr. F. C., O.B.E.—Elected to a Fellowship of the Imperial College of Science and Technology.
- LEWIS, ESSINGTON.—Appointed Director-General of Munitions and Aircraft Production in Australia. Appointed a Companion of Honour. Elected an Honorary Member of the American Institute of Mining and Metallurgical Engineers.

- LOWE, E. J.—Created an Officer of the Order of the British Empire.
- MERICA, Dr. P. D.—Elected an Honorary Member of the American Institute of Mining and Metallurgical Engineers.
- PERRY, R. P.—Created an Officer of the Order of the British Empire.
- RIPLEY, L. H.—Created an Officer of the Order of the British Empire.
- ROBSON, STANLEY.—Elected a Member of Council of the Institute of Metals.
- SANKEY, Colonel H. B.—Created a Commander of the Order of the British Empire.
- STIRLING, A.—Appointed Honorary Technical Adviser to the Directorate of Gas and Heat Supplies (Ministry of Supply).
- TENNENT, JAMES.—Appointed a Deputy-Lieutenant of the County of Lanark. Appointed an Honorary Sheriff-Substitute of Lanarkshire at Airdrie.
- THOMAS, B.—Elected President of the Staffordshire Iron and Steel Institute.
- WARDROBE, F.—Elected President of the Sheffield Society of Engineers and Metallurgists for 1944.
- WOOD, W. W.—Re-elected Master Cutler; fifth term of office.
- WRIGHT, L. F.—Re-elected President of the Cleveland Institution of Engineers.
- WYLLIE, Sub-Lieut. M. R. J.—Received the degree of D.Phil. (Oxon.).

#### STAFF.

The Secretary resigned his position as Deputy-Controller of the Chrome Ore, Magnesite and Wolfram Control and associated Controls of the Ministry of Supply as from 31st October, 1943, and by permission of the Council accepted an appointment in an honorary consultative capacity with the Iron and Steel Control.

Captain H. Davison was promoted to Major in the Pioneer Corps, and Miss J. Best joined the Auxiliary Territorial Service.

Miss G. Davison, Assistant Librarian, completed 25 years' service with the Institute.

The Council again wish to record their appreciation of the services rendered by the staff.

#### SUPPLY AND TRAINING OF METALLURGISTS.

A report and evidence were submitted to the committee set up by the Advisory Council of the Department of Scientific and Industrial Research to consider steps required to secure an increased and adequate supply of metallurgists.

## MEETINGS.

### *Annual Meeting.*

The Annual Meeting was held at the offices of the Institute, 4, Grosvenor Gardens, London, S.W.1, on Thursday, 13th May, 1943, at 2.45 P.M. Mr. James Henderson, President, was in the Chair. Fifteen papers, including ten submitted under the auspices of Joint Research Committees of the Institute and the British Iron and Steel Federation, were presented, and two papers were discussed at the meeting.

### *Autumn Meeting.*

The Autumn Meeting was also held at the offices of the Institute on Thursday, 14th October, 1943, with the President, Mr. James Henderson, in the Chair. There were two sessions, commencing at 11 A.M. and 2.45 P.M., respectively. Fourteen papers were presented, including seven submitted by Joint Research Committees of the Institute and the British Iron and Steel Federation, and five were discussed at the meeting.

## RELATIONS WITH OTHER SOCIETIES AND TECHNICAL INSTITUTIONS.

Friendly relations were maintained with scientific societies and technical institutions in Great Britain, the Dominions and in allied and neutral countries. Certain activities continued as formerly to be carried on jointly with The Institute of Metals, and a number of committees of the two Institutes are collaborating in studying problems of mutual interest. As recorded elsewhere, the Council invited the President of that Institute to become an Honorary Member of Council during his period of office and this invitation was accepted and a similar invitation issued to the President of The Iron and Steel Institute. A number of joint meetings were again held with other scientific societies and technical institutions in Great Britain. The Council record in particular their pleasure at the continued friendly relations existing with the following societies on the same basis as in previous years :

- Cleveland Institution of Engineers.
- Ebbw Vale Metallurgical Society.
- Lincolnshire Iron and Steel Institute.
- Manchester Metallurgical Society.
- Newport and District Metallurgical Society.
- Sheffield Metallurgical Association.
- Sheffield Society of Engineers and Metallurgists.
- Staffordshire Iron and Steel Institute.
- Swansea Technical College Metallurgical Society.
- West of Scotland Iron and Steel Institute.

*Joint Meetings.*

(For the period from 1st April, 1943, to 31st March, 1944.)

The following are particulars of Joint Meetings held with Local Societies (up to 31st March, 1944) :

**Wednesday, 29th September, 1943 : Manchester Metallurgical Society and the Institute of Metals.**

*Place and Time* : The Engineer's Club, Albert Square, Manchester, at 6.30 p.m.

*Chairman* : Mr. L. E. Benson, M.Sc., President of the Manchester Metallurgical Society.

*Lecture* : "Lattice Structures in Relation to Physical Properties of Metals," by Dr. W. H. Taylor.

**Saturday, 30th October, 1943 : Newport and District Metallurgical Society.**

*Place and Time* : The Newport Technical College, Newport, at 6 p.m.

*Chairman* : Mr. G. H. Latham, J.P., President of the Newport and District Metallurgical Society and Member of Council of The Iron and Steel Institute.

*Lecture* : "The Yield Point in Steel and its Significance," by Principal C. A. Edwards, D.Sc., F.R.S.

**Tuesday, 23rd November, 1943 : The Lincolnshire Iron and Steel Institute.**

*Place and Time* : The Modern School, Cole Street, Scunthorpe, at 7.30 p.m.

*Chairman* : Mr. J. N. Kilby, President of the Lincolnshire Iron and Steel Institute and Honorary Member of Council of The Iron and Steel Institute.

*Paper* : "A Review of Basic Open-Hearth Practice at an Australian Plant," by Mr. R. L. Knight. (Presented by Mr. A. Robinson, Chairman of the Open-Hearth Committee.)

**Saturday, 4th December, 1943 : The Sheffield Society of Engineers and Metallurgists and the Sheffield Metallurgical Association.**

*Place and Time* : Assembly Room, Royal Victoria Station Hotel, Sheffield, at 2.30 p.m.

*Chairman* : Professor J. H. Andrew, Past-President of the Sheffield Society of Engineers and Metallurgists and Member of Council of The Iron and Steel Institute.

*Report* : "Fourth Report of the Oxygen Sub-Committee." (Presented by Dr. T. Swinden, Chairman of the Sub-Committee.)

**Monday, 13th December, 1943 : The Cleveland Institution of Engineers.**

*Place and Time* : The Cleveland Scientific and Technical Institute, Corporation Road, Middlesbrough, at 6.30 p.m.

*Chairman* : Mr. L. F. Wright, President of The Cleveland Institution of Engineers and Honorary Member of Council of The Iron and Steel Institute.

*Paper* : "The Use of Basic-Lined Ladles in the Desulphurisation of Cast Iron by Sodium Carbonate," by N. L. Evans, B.Sc., A.I.C.

**Tuesday, 11th January, 1944 : The Staffordshire Iron and Steel Institute.**

*Place and Time :* Dudley and Staffordshire Technical College,  
The Broadway, Dudley, at 7 p.m.

*Chairman :* Mr. Bernard Thomas, President of The Staffordshire Iron and Steel Institute and Honorary Member of Council of The Iron and Steel Institute.

*Paper :* "A Study of Austenitic Grain Growth in Medium-Carbon Steels," by J. H. Whiteley, F.I.C.

**Thursday, 13th January, 1944 : The Ebbw Vale Metallurgical Society.**

*Place and Time :* The Rational Hall, Ebbw Vale, at 7 p.m.

*Chairman :* Mr. W. H. R. Bird, M.A., B.Sc., Chairman of the Ebbw Vale Metallurgical Society.

*Lecture :* "Research in the Steel Industry," by Dr. C. H. Desch, F.R.S.

**Monday, 13th March, 1944 : The Cleveland Institution of Engineers.**

*Place and Time :* The Cleveland Scientific and Technical Institute, Corporation Road, Middlesbrough, at 6.30 p.m.

*Chairman :* Mr. L. F. Wright, President of the Cleveland Institution of Engineers and Honorary Member of Council of The Iron and Steel Institute.

*Paper :* "A Review of Basic Open-Hearth Practice at an Australian Plant," by Mr. R. L. Knight. (Presented by Mr. A. Robinson, Chairman of the Open-Hearth Committee.)

On Wednesday, 3rd March, 1943, Dr. S. W. Smith, C.B.E., gave a lecture to commemorate the centenary of the birth of Sir W. C. Roberts-Austen at a meeting organised by The Institution of Mechanical Engineers in conjunction with the Institute of Metals and The Iron and Steel Institute and held at the offices of the Institution, Storey's Gate, London, S.W.1, commencing at 5.30 p.m. Professor F. C. Lea, O.B.E., D.Sc., President of The Institution of Mechanical Engineers, was in the Chair, and was supported by Sir John Greenly, K.C.M.G., C.B.E., M.A., President of the Institute of Metals, and Mr. James Henderson, President of The Iron and Steel Institute.

Members of the Institute were invited to attend and take part in the discussion of papers presented at the Annual Meeting of the Institute of British Foundrymen, held at the Waldorf Hotel, Aldwych, London, on Saturday, 26th June, 1943. During the morning session Dr. S. F. Dorey gave a lecture on "The Contribution of the Steel Founder to Marine Engineering," and in the afternoon papers by C. W. Briggs on "Hot Tears in Steel Castings," by L. W. Bolton and J. Hill on "The Continuous Production of Manganese Steel Castings from the Tropenas Converter," and by E. Derek Wells and A. Johnson on "A War-Time Steel Foundry—Some Problems and Developments" were presented.

On Friday, 18th June, 1943, a meeting of the Applied Mechanics

Group of the Institution of Mechanical Engineers was held at the offices of that Institution, Storey's Gate, London, S.W.1, at 5.30 P.M. A paper by Dr. H. O'Neill on "The Significance of Tensile and other Mechanical Test Properties of Metals" was presented, and Members of The Iron and Steel Institute were invited to be present.

On Friday, 10th December, 1943, the Joint Committee of Materials and their Testing organised a meeting at 5.30 P.M. at the offices of the Institution of Mechanical Engineers, Storey's Gate, London, S.W.1, at which the following papers on plastics were presented : "A Survey of Plastics from the Viewpoint of the Mechanical Engineer," by Dr. S. L. Smith, and "Moulding Plant for Plastics," by J. L. Daniels. Members of The Iron and Steel Institute were invited to be present.

The meetings were well supported and the discussions interesting. The Council desire once again to record their thanks to the Presidents, Councils and Secretaries of the Local Societies, as well as to the authors of the papers.

#### PUBLICATIONS.

*Papers and Committee Reports.*—Two volumes of the *Journal* and Special Report No. 29, "Review of the Work of the Joint Research Committees, 1924–1943, of The Iron and Steel Institute and the British Iron and Steel Federation," were published during the year. The two issues of the *Journal* contain fifteen papers issued under the auspices of the Joint Research Committees of The Iron and Steel Institute and The British Iron and Steel Federation, two Sub-Committee Reports and twelve papers, as follows :

- "First Report of the Marine Corrosion Sub-Committee." (Paper No. 9/1943 of the Corrosion Committee (submitted by the Marine Corrosion Sub-Committee).)
- "Fourth Report of the Oxygen Sub-Committee." (Paper No. 22/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Oxygen Sub-Committee).)
- C. R. BARBER : "The Calibration of the Platinum/13%-Rhodium-Platinum Thermocouple over the Liquid Steel Temperature Range." (Paper No. 17/1942 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Liquid Steel Temperature Sub-Committee).)
- A. J. COOK and F. W. JONES : "The Brittle Constituent of the Iron-Chromium System (Sigma Phase). I.—A Survey of the Limits of the Sigma Phase in the Binary System." (Paper No. 11/1943 of the Alloy Steels Research Committee (submitted by Dr. C. Sykes, F.R.S.).)
- W. DAVIES and W. J. REES : "British Resources of Steel Moulding Sands." (Paper No. 4/1943 of the Steel Castings Research Committee (submitted by the Moulding Materials Sub-Committee).)
- C. A. EDWARDS, F.R.S., D. L. PHILLIPS and Y. H. LIU : "The Yield Point in Steel."
- J. C. HUDSON : "Present Position of the Corrosion Committee's Field Tests on Atmospheric Corrosion (Unpainted Specimens)." (Paper No. 10/1943 of the Corrosion Committee.)
- A. JACKSON : "The Maintenance of the Furnace Linings in Large Basic Open-Hearth Tilting Furnaces by the use of Chrome Ore, Magnesite and Serpentine."

- R. L. KNIGHT : "A Review of Basic Open-Hearth Practice at an Australian Plant."
- T. LAND : "Thermal Stresses in Ingot Moulds." (Paper No. 20/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Stresses in Moulds Panel of the Ingot Moulds Sub-Committee, a Joint Sub-Committee of the Heterogeneity and Open-Hearth Committees).)
- F. LÁSZLÓ : "Tessellated Stresses.—Part I."
- F. LÁSZLÓ : "Tessellated Stresses.—Part II."
- F. LÁSZLÓ : "Graphitisation of Steel Influenced by Tessellated Stresses."
- E. F. LAW and VERNON HARBORD : "The Solidification and Cooling of Steel Ingots. Notes on an Examination of Three Typical Ingots." (Paper No. 21/1943 of the Committee on the Heterogeneity of Steel Ingots.)
- R. H. MYERS : "A Review of the Work of the Ingot Moulds Sub-Committee." (Paper No. 19/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Ingot Moulds Sub-Committee, a Joint Sub-Committee of the Heterogeneity and Open-Hearth Committees).)
- L. NORTHCOTT and D. MCLEAN : "The Structure and Segregation of two Ingots of Ingot Iron, one Containing Lead."
- T. W. PARKER and R. W. NURSE : "Merwinite in the System CaO-MgO-SiO<sub>2</sub>."
- N. J. PETCH : "The Positions of the Carbon Atoms in Martensite."
- A. PREECE : "The Desirability of Removing Sulphur from Gaseous Fuels for Heating Ferrous Metal." (Paper No. 10/1943 of the Alloy Steels Research Committee.)
- T. H. SCHOFIELD : "Note on some Precipitation Effects Observed in Mild-Steel and Wrought-Iron Pipe."
- G. C. SEAGER, and F. C. THOMPSON : "The Influence of Temperature on the Modulus of Elasticity of some Plain Carbon and Alloy Steels." (Paper No. 9/1943 of the Alloy Steels Research Committee.)
- H. T. SHIRLEY and E. ELLIOTT : "A Critical Consideration of some Applications of the Spectrograph to Steelworks Analysis." (Paper No. 18/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by Dr. W. H. Hatfield, F.R.S.).)
- L. R. STANTON : "A Recording Dilatometer for Metal Specimens." (Paper No. 7/1942 of the Alloy Steels Research Committee (submitted by Professor F. C. Thompson).)
- N. STUART and U. R. EVANS : "The Effect of Zinc on the Corrosion-Fatigue Life of Steel." (Paper No. 8/1943 of the Corrosion Committee.)
- T. SWINDEN : "Leaded Manganese-Molybdenum Steel." (Paper No. 13/1943 of the Alloy Steels Research Committee.)
- F. C. THOMPSON and N. C. SAHA : "Thermo-Electric Power of very Pure Iron Between 20° and 230° C." (Paper No. 8/1943 of the Alloy Steels Research Committee.)
- F. V. WARNOCK and J. B. BRENNAN : "Some Tensile Shock Properties of Carbon Steels."
- J. WHITE : "The Physical Chemistry of Open-Hearth Slags."
- J. H. WHITELEY : "A Study of Austenitic Grain Growth in Medium-Carbon Steels." (Paper No. 12/1943 of the Alloy Steels Research Committee.)

*The Bulletin of The Iron and Steel Institute* was published monthly during the year; as usual, it was reprinted as Section II. of the *Journals* issued for the corresponding periods. The *Bulletin* is supplied free of charge to Members on application; the sub-

scription rate to non-members is 30s. per annum (\$6 to members of the American Iron and Steel Institute, the American Institute of Mining and Metallurgical Engineers and the American Society for Metals).

*Translation Service.*—Translations of forty-eight foreign technical papers were included in the Institute's Translation Series; they are obtainable by Members at 10s. each (5s. for each additional copy of the same translation). Arrangements were made with a number of Companies, Research Associations and Government Departments by which translations prepared by them are made available to Members through the Service and the Council wish to record their appreciation at the facilities thus made available.

Members requiring translations of foreign technical papers are invited to communicate with the Secretary. Those that are suitable will be included in the Translation Series and will be supplied at the rates indicated above; it may be possible to prepare others at the Member's expense.

In recent volumes of the *Journal* the translations issued during the period covered by the volume have been listed on pages preceding the title page.

#### JOINT LIBRARY AND INFORMATION DEPARTMENT.

##### *Joint Library.*

The work of the library, which is organised jointly between the Institute and the Institute of Metals, was well maintained. A number of useful additions were made, and the Council wish to take this opportunity of thanking those from whom presentations were received. A list of additions made to the library is issued quarterly and copies will be sent to Members on request. Demands for the loan of books and periodicals again showed an increase; 6430 publications were borrowed by Members, Companies and Government departments in 1943, this being an increase of 2% on the record figure of the previous year and an increase of over 50% over the pre-war figure.

The majority of the articles abstracted in the monthly *Bulletin* of The Iron and Steel Institute are filed in the Joint Library and are available for loan. In addition, photographic copies of articles can be supplied under certain conditions.

##### *Micro-Film Service.*

The service for the supply of micro-films in conjunction with ASLIB and the Science Library, South Kensington, continued in operation. By the generosity of the Rockefeller Foundation a number of reading instruments had in the previous year been placed at the disposal of the Royal Society. One of these instruments was allocated to The Iron and Steel Institute and placed in

the Joint Library, so that it is now possible for Members and representatives of Companies either to read micro-films in the reading room or to obtain them for use with their own instruments. Members in possession of micro-film copies of foreign technical journals are invited to deposit them in the Library and to give permission to make them available to others wishing to inspect them.

*Collaboration with the Institute of Civil Engineers and the Science Library.*

The valuable collections of scientific works included in the Science Library and the Library of The Institution of Civil Engineers are available for consultation or loan under certain conditions. Members who wish to avail themselves of these facilities should communicate with the Librarian of the Joint Library, 4 Grosvenor Gardens, London, S.W.1.

*Information Department.*

Members seeking information on technical subjects are invited to avail themselves of the information service. The increased number of enquiries dealt with during the past year is an indication of the value of the service. The shortage of staff has been a serious problem, but it is hoped that enquiries will continue to be answered with as little delay as possible.

**RESEARCH.**

Active collaboration with the Iron and Steel Industrial Research Council was continued on the same basis as in former years, the various Research Committees having been engaged on full programmes. In a Special Report (No. 29), "Review of the Work of the Joint Research Committees, 1924-1943," their work and current programmes were briefly described.

The research activities of the Institute suffered a severe loss during the year owing to the death of Dr. W. H. Hatfield, F.R.S., the Chairman since their inception of the Heterogeneity of Steel Ingots Committee, the Corrosion Committee and the Alloy Steels Research Committee. Dr. T. Swinden, Vice-Chairman, was elected to succeed Dr. Hatfield as Chairman of these Committees, and Mr. H. H. Burton, Dr. T. Swinden and Mr. W. J. Dawson were invited to become Chairmen in his place of the Hair-Line Crack, Special Aero-Components and Inclusions Sub-Committees, respectively.

The following is a list of the Joint Committees of the Institute and the British Iron and Steel Federation, reporting to the Iron and Steel Industrial Research Council, and of their Sub-Committees; the number of meetings recorded in 1943 was 62 (56 in 1939; 59 in 1940; 64 in 1941; 75 in 1942) :

**Alloy Steels Research Committee:** Chairman, Dr. T. Swinden. Established June, 1934. Meetings held during 1943 : four.

*Thermal Treatment Sub-Committee :* Chairman, Mr. P. B. Henshaw. Established January, 1936. Meetings held during 1943 : two.

*Hair-Line Crack Sub-Committee :* Chairman, Mr. H. H. Burton. Established July, 1938. Meetings held during 1943 : four.

*Special Aero-Components Sub-Committee :* Chairman, Dr. T. Swinden. Established July, 1940. Meetings held during 1943 : (not recorded).

**Corrosion Committee :** Chairman, Dr. T. Swinden. Established July, 1928. Meetings held during 1943 : three.

*Laboratory (Corrosion) Research Sub-Committee :* Chairman, Dr. U. R. Evans; Acting Chairman, Dr. G. D. Bengough, F.R.S. Established June, 1930. No meetings held during 1943 ; activities carried on by correspondence.

*Protective Coatings Sub-Committee :* Chairman, Mr. T. M. Herbert. Established January, 1936. Meetings held during 1943 : two.

*Marine Corrosion Sub-Committee :* Chairman, Dr. G. D. Bengough, F.R.S. Re-formed, November, 1938. Meetings held during 1943 : five.

*Sub-Committee on Low-Alloy Steels :* Established June, 1938. No meetings held during 1943 ; activities carried on by correspondence.

*Sub-Committee on the Corrosion of Buried Metals (working in collaboration with the Committee on Soil Corrosion of Metals and Cement Products of The Institution of Civil Engineers) :* Established October, 1937. No meetings held during 1943, but two meetings of Members and representatives of tube and pipe manufacturers took place.

**Heterogeneity of Steel Ingots Committee :** Chairman, Dr. T. Swinden. Established May, 1924. Meetings held during 1943 : four.

*Ingots Moulds Sub-Committee (formed jointly by the Committee on the Heterogeneity of Steel Ingots and the Open-Hearth Committee of the Iron and Steel Industrial Research Council) :* Chairman, Mr. R. H. Myers. Established November, 1934. Meetings held during 1943 : one. (Stresses in Moulds Panel, none).

*Joint Sub-Committee on the Physical Chemistry of Steelmaking (formed jointly by the Committee on the Heterogeneity of Steel Ingots and the Open-Hearth Committee of the Iron and Steel Industrial Research Council) :* Chairman, Dr. T. Swinden. Established, 1938. No meetings held during 1943.

*Liquid Steel Temperature Sub-Committee :* Chairman, Mr. E. W. Elcock. Established March, 1929. Meetings held during 1943 : two.

*Oxygen Sub-Committee :* Chairman, Dr. T. Swinden. Established January, 1936. No meetings held during 1943 (Chemists' Panel, two).

*Inclusions Sub-Committee* : Chairman, Mr. W. J. Dawson. Established November, 1936. Meetings held during 1943 : four.

*Standard Methods of Analysis Sub-Committee* : Chairman, Dr. E. Gregory. Established September, 1939. Meetings held during 1943 : eight.

**Steel Castings Research Committee** : Chairman, Mr. W. J. Dawson. Established November, 1934. Meetings held during 1943 : six.

*Moulding Materials Sub-Committee* : Chairman, Dr. W. J. Rees. Established March, 1936. Meetings held during 1943 : three.

*Foundry Practice Sub-Committee* : Chairman, Mr. F. Cousins. Established May, 1938. Meetings held during 1943 : five.

*Foundry Steel Temperature Sub-Committee* : Chairman, Mr. D. A. Oliver. Established December, 1941. Meetings held during 1943 : two.

*Side-Blown Converter Practice Sub-Committee* : Convenor, Dr. T. P. Colelough. Established September, 1943. Meetings held during 1943 : three.

#### APPOINTMENT OF REPRESENTATIVES.

The following is a list of the Institute's representatives on various governing bodies and committees for the year 1944; it has been brought up to date to 31st March, 1944 :

**BRITISH CAST IRON RESEARCH ASSOCIATION** : Professor T. Turner.

**BRITISH CORPORATION REGISTER OF SHIPPING AND AIRCRAFT**, Technical Committee : Dr. A. McCance, F.R.S.

**BRITISH ELECTRICAL AND ALLIED INDUSTRIES RESEARCH ASSOCIATION**,

Sub-Committee J/E, Joint Committee, Steels for High Temperatures : Dr. T. Swinden (*one appointment open*).

Sub-Committee J, Earthing to Water Mains : Dr. J. C. Hudson.

**BRITISH IRON AND STEEL FEDERATION**, Statistical Committee : Mr. K. Headlam-Morley.

**BRITISH REFRACTORIES RESEARCH ASSOCIATION**, Council : Mr. W. J. Brooke, J.P.

**BRITISH STANDARDS INSTITUTION**,

Chemical Engineering Divisional Council : Mr. E. F. Law.

Engineering Divisional Council E/- : Dr. T. Swinden, Mr. K. Headlam-Morley and Mr. R. Mather.

Sub-Committee M33/7, Protective Glasses for Welders and Industrial Purposes : Dr. C. H. Desch, F.R.S.

Sub-Committee C/25/10, Painting of Iron and Steel : Mr. F. Fancutt, Mr. R. A. Hacking.

Technical Committee CEB/1, Cement : Mr. W. J. Brooke, J.P.

- Technical Committee CEB/6/1, Concrete Blocks : Mr. W. J. Brooke, J.P.
- Technical Committee CH/17, Symbols used in Diagrams of Chemical Engineering Plant : Mr. A. E. Chattin.
- Technical Committee EL/28, Fans : Mr. A. F. Webber.
- Iron and Steel Industry Committee IS/- : Dr. T. Swinden.
- Technical Committee IS/1, Co-ordination of Iron and Steel Specifications : Dr. T. Swinden.
- Technical Committee IS/6, Steel Castings : Dr. R. H. Greaves.
- Technical Committee IS/8, Creep Properties : *appointment open.*
- Technical Committee IS/15, Iron and Steel for Shipbuilding : Sir Edward J. George.
- Technical Committee IS/17, Cast Iron Columns for Street Lighting : Mr. J. G. Pearce.
- Technical Committee IS/35, Cast Iron : Mr. J. G. Pearce.
- Technical Committee IS/35/3, Malleable Steel Castings : Mr. C. H. Kain.
- Technical Committee ME/23, Brinell Hardness Testing : *appointment open.*
- Technical Committee ME/25, Testing of Thin Metal Sheet and Strip : Dr. T. Swinden.
- Technical Committee ME/32, Engineering Symbols and Abbreviations : Dr. T. Swinden.
- Solid Fuel Industry Committee, SF/- : Mr. A. F. Webber.
- Technical Committee SF/1, Nomenclature and Definitions : Mr. A. F. Webber.
- Technical Committee SF/2, Underfed Screw Type Stokers : Mr. A. F. Webber.
- Technical Committee SF/4, Heating Stoves : Mr. A. F. Webber.
- Technical Committee CH/18/2, Metallic Finishes : Mr. F. C. Platt.
- Units and Technical Data Co-ordinating Committee : Sir Wm. Larke, K.B.E.
- CITY AND GUILDS OF LONDON INSTITUTE, Advisory Committee on Metallurgy : Mr. E. C. Greig.
- CONSTANTINE COLLEGE, Advisory Committee : Mr. E. W. Jackson.
- EMPIRE COUNCIL OF MINING AND METALLURGICAL INSTITUTIONS : Mr. K. Headlam-Morley, Mr. J. Sinclair Kerr.
- ENGINEERING PUBLIC RELATIONS COMMITTEE,
- Main Committee : Mr. James Henderson.
- Executive Committee : Mr. K. Headlam-Morley.
- HONG-KONG UNIVERSITY, Home Committee : *appointment open.*
- IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, Board of Governors : Mr. James Henderson.
- IMPERIAL INSTITUTE, Mineral Resources Department, Iron and Ferro-Alloy Metals Committee : Mr. K. Headlam-Morley.

INSTITUTE OF FUEL, Council : Dr. R. J. Sarjant.

INSTITUTE OF WELDING, Council and Representative of Patron Institution : Mr. K. Headlam-Morley.

INSTITUTION OF MECHANICAL ENGINEERS, Research Committee on High-Duty Cast Irons for General Engineering Purposes : Dr. J. E. Hurst.

IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL : Mr. K. Headlam-Morley, the Hon. R. G. Lyttelton (*one appointment open*).

JOINT COMMITTEE ON MATERIALS AND THEIR TESTING : Mr. K. Headlam-Morley.

LIVERPOOL UNIVERSITY, Court of Governors : Sir W. Peter Rylands, Bt.

LLOYD'S REGISTER OF SHIPPING, Technical Committee : Mr. James Henderson, Mr. P. Baxter.

NATIONAL PHYSICAL LABORATORY, General Board : Professor J. H. Andrew, Dr. T. Swinden.

PARLIAMENTARY AND SCIENTIFIC COMMITTEE : Mr. K. Headlam-Morley.

RAMSAY MEMORIAL LABORATORY, Advisory Committee : *appointment open*.

ROYAL SCHOOL OF MINES, Advisory Board : Mr. Vernon Harbord.

ROYAL SOCIETY, General Board for Administering Government Grants for Scientific Investigations : The President.

SCHOOL OF METALLIFEROUS MINING (CORNWALL), Board of Governors : Mr. J. S. Hollings, C.B.E.

SCIENCE MUSEUM, Advisory Council : Mr. James Henderson.

SHEFFIELD UNIVERSITY, Court of Governors : Sir Arthur B. Winder, J.P.



## STEEL INSTITUTE.

31ST DECEMBER, 1943.

of the Institute and certify it to be correct.

(Signed) W. B. KEEN & Co.  
*Chartered Accountants.*

# THE IRON AND INCOME AND EXPENDITURE ACCOUNT

# STEEL INSTITUTE.

FOR THE YEAR ENDED 31ST DECEMBER, 1943.

## EXPENDITURE.

1942.							
£	s.	£	s.	d.	£	s.	d.
7,121		Salaries (including Pensions and Overtime)	...	7,048	15	4	
403		Staff in H.M. Forces	...	508	18	0	
476		War Bonus	...	750	2	3	
8,000					8,307	15	7
875		Less Contribution from Ministry of Supply	...	687	10	0	
150		Do. Carnegie Research Fund	...	150	0	0	
					837	10	0
—	6,975	National Insurance	...				7,470
60		Staff Superannuation Fund	...				63
405		Office Rent	...				7
1,200		Repairs, Decorations and A.R.P.	...				0
80		Cleaning, Heating, Lighting and Water	...				1
888		Library Books and Binding	...				54
490		Office Furniture	...				829
30		Annual Meeting	...				16
27		Autumn Meeting	...				10
43		Publishing Expenses:—					394
1,416		Journal: Printing and Paper	...	1,398	13	10	19
142		Postage	...	172	3	6	7
138		Advance Copies: Printing	...	275	9	5	0
41		Postage	...	134	13	6	10
459		Bulletin: Printing	...	452	19	3	6
64		Postage	...	69	17	4	1
6		Bibliographies	...	10	16	6	0
245		Translation Service	...	118	19	0	4
—	2,511	Stationery and Printing	...				2,633
548		Postage and Receipt Stamps	...				579
586		Travelling and Entertainment Expenses	...	393	12	0	8
429		Less Recoverable from Ministry of Supply	...	102	6	4	2
104							652
—	325	Insurance	...	57	14	10	3
60		Do. War Damage	...	90	3	3	0
101							291
161		Auditors' Fee for 1942	...				5
44		Telephone Rental and Calls	...				8
204		Office Disbursements and Sundry Expenses	...				1
238							52
		Grants:—					192
50		British Electrical and Allied Industries Research Association	...	50	0	0	0
25		British Refractories Research Association	...	25	0	0	11
1		Joint Committee on Materials and their Testing	...	1	1	0	1
50		British Standards Institution	...	50	0	0	0
10		Mellor Memorial	...	10	0	0	0
10		Parliamentary and Scientific Committee	...	10	10	0	0
—		Foundry Prize—Sheffield University	...	10	10	0	0
		Sundry Researches	...	50	0	0	0
—	146	Iron and Steel Industrial Research Council—Grant	...				207
2,500							1
—	£17,461						0
3,296		Balance brought down	...				2,500
		Transfer Reserve and Suspense Account:—					0
539		Repairs and Decorations	...	300	0	0	
250		Library	...	200	0	0	
50		Ten-Year Index	...	50	0	0	
—		General Reserve	...	500	0	0	
25		Bessemer Gold Medal	...	25	0	0	
—	864	Companies' Nominations:—					1,075
82		Entrance Fees	...	184	16	0	0
117		Subscriptions Account:—					
5		Home Members	...	274	1	0	
10		Overseas Members	...	15	15	0	
		Associates	...	24	3	0	
—	214	Balance, being excess of Income over Expenditure	...	313	19	0	498
132							15
—	£4,506						2
							214
							15
							2
							£4,413
							17
							0

WILLIAMS

BALANCE SHEET,

LIABILITIES.

1942.				£ s. d.		£ s. d.	
	£	£					
2,220		Capital Value representing Market value of £3,000 3½% Conversion Loan at 21st September, 1926, when Fund was inaugurated ... ... ...				2,220	0 0
—		Bank Overdraft—Current Account ... ... ...				72	6 9
75		Income and Expenditure Account:— Balance as at 1st January, 1943 ... ... ...		696	5 5		
121		Less Excess of Expenditure over Income for the year to 31st December, 1943 ... ... ...		79	12 0		
696						616	13 5
£2,916						£2,909	0 2

INCOME AND EXPENDITURE ACCOUNT FOR  
INCOME.

1942.				£ s. d.		£ s. d.	
	£	£					
120	Interest on 3½% Conversion Loan	... ... ...		... ...		120	16 10
1	Interest on Deposit	... ...				5	1 11
—	Excess of Expenditure over Income for the year	... ...		... ...		79	12 0
£121						£205	10 9

ANDREW CARNEGIE  
BALANCE SHEET,

LIABILITIES.

1942.				£ s. d.		£ s. d.	
	£	£					
100	Sundry Creditors:— Grants ...	... ...		220	0 0		
10	Auditors' Fees	... ...		10	10 0		
—						230	10 0
110	Amount due to General Fund	... ...				136	0 0
136	General Reserve	... ...				500	0 0
21,241	Amount of Original Fund (\$100,000)	... ...		21,241	5 6		
2,912	Add Amounts since capitalised per last Balance Sheet	... ...		4,440	13 0		
						25,681	18 6
1,529	Add Profit on Sales of Investments		£ s. d.				
3,351	Add Surplus Income as at 1st January, 1943	... 4,196	2 0				
845	Add Excess of Income over Expenditure for the year ...	399	17 10			4,595	19 10
—							
29,878						30,277	18 4
£30,124						£31,144	8 4

INCOME AND EXPENDITURE ACCOUNT FOR  
INCOME.

1942.				£ s. d.	
	£	£			
1,195	Interest on Investments (Gross)	... ...		1,212	5 9
10	Interest on Deposit	... ...		3	12 10

£1,205

£1,215 18 7

## PRISE FUND.

31ST DECEMBER, 1943.

### ASSETS.

1942.	£	£		£	s.	d.
2,670	£3,452 15s. 7d.	3½%	Conversion Loan (at cost)	...	...	2,670 0 0
	Cash at Bank :—					
59	P.O. Savings Bank Account	...	...	...	...	239 0 2
187	Current Account	...	...	...	...	—
246						
	£2,916			£2,909	0	2

THE YEAR ENDED 31ST DECEMBER, 1943.

### EXPENDITURE.

1942.	£	£		£	s.	d.
	Awards	...	...	...	200	0 0
	Legal Expenses	...	...	...	5	10 9
121	Excess of Income over Expenditure for the year	...	...	...	—	
£121				£205	10	9

## RESEARCH FUND.

31ST DECEMBER, 1943.

### ASSETS.

1942.	£	£		£	s.	d.
28,688	Investments at cost per Schedule	...	...	29,938	0	5
	(The Market value of these Investments at 31st December, 1943, was £35,159 15s. 0d.)					
	Cash at Bank :—					
368	On Current Account	...	...	22	6	4
454	On Deposit Account	...	...	956	5	1
389	P.O. Savings Bank Account	...	...	11	4	9
1,211	Income Tax Recoverable	...	...	989	16	2
225				216	11	9
	£30,124			£31,144	8	4

THE YEAR ENDED 31ST DECEMBER, 1943.

### EXPENDITURE.

1942.	£	£		£	s.	d.
300	Scholarship Grants	...	...	200	0	0
150	Less Grant Returned	...	...	50	0	0
150	Printing Reports	...	...	150	0	0
150	Contribution to General Fund on account of Salaries	...	...	150	0	0
10	Audit Fee	...	...	10	10	0
—	Legal Expenses	...	...	5	10	9
—	General Reserve—Amount set aside	...	...	500	0	0
845	Balance, being Excess of Income over Expenditure for the year	...	...	399	17	10
£1,205				£1,215	18	7

THE IRON AND STEEL INSTITUTE.

SCHEDULE OF INVESTMENTS AT 31ST DECEMBER, 1943.

SHOWING NOMINAL VALUES, COST VALUES AND PRESENT MARKET VALUES.

Nominal Value.	Market Value, 31st December, 1913.	Cost Value.	Nature of Security.		GENERAL FUND OF THE INSTITUTE.						LIFE COMPOSITION FUND.					
			s. d.	s. d.	£	s. d.	£	s. d.	£	s. d.	£	s. d.	£	s. d.	£	s. d.
2,197 7 0	3½% War Stock	...	...	...	...	...	...	...	...	...	2,271 10 3	2,161 0 8	615 12 2	513 2 3	587 18 10	53,385 14 2
1,324 7 4	3½% Conversion Loan	...	...	...	...	...	...	...	...	...	1,387 5 6	1,253 14 0	169 6 5	168 0 0	1,324 7 4	1,324 7 4
1,447 0 0	Southern Railway 4% Redeemable Debenture Stock	...	...	...	...	...	...	...	...	...	1,480 10 6	1,449 2 4	1,083 19 0	1,254 17 6	1,447 0 0	1,447 0 0
1,872 0 0	London & North Eastern Railway 4% 2nd Guaranteed Stock	...	...	...	...	...	...	...	...	...	1,684 16 0	9,149 13 3	703 17 10	638 6 1	1,872 0 0	1,872 0 0
2,241 0 0	Do. 4% 1st do.	...	...	...	...	...	...	...	...	...	2,207 7 8	2,431 14 5	212 14 5	211 8 10	2,241 0 0	2,241 0 0
649 4 0	2½% Consolidated Stock	...	...	...	...	...	...	...	...	...	2,106 2 3	1,800 0 0	771 19 4	600 0 0	649 4 0	649 4 0
1,500 1 0	Buenos Ayres Great Southern Railway 4% Debenture Stock	...	...	...	...	...	...	...	...	...	922 10 0	1,314 12 9	3,242 1 5	3,175 18 1	1,500 1 0	1,500 1 0
964 1 0	4% Consolidated Stock	...	...	...	...	...	...	...	...	...	3,242 1 5	3,242 1 5	3,242 1 5	3,242 1 5	964 1 0	964 1 0
437 0 0	London & North Eastern Railway 3% Debenture Stock	...	...	...	...	...	...	...	...	...	356 3 1	376 12 5	13,865 3 1	13,865 3 1	437 0 0	437 0 0
2,242 19 3	Funding Loan 1960/90	...	...	...	...	...	...	...	...	...	13,865 3 1	9,512 7 7	1,010 0 0	1,000 0 0	2,242 19 3	2,242 19 3
1,000 0 0	3% Defence Bonds (Post Office Register)	...	...	...	...	...	...	...	...	...	1,010 0 0	1,000 0 0	2,020 0 0	2,000 0 0	1,000 0 0	1,000 0 0
2,000 0 0	3% Savings Bonds 1945/65	...	...	...	...	...	...	...	...	...	2,020 0 0	2,000 0 0	2,020 0 0	2,000 0 0	2,000 0 0	2,000 0 0
											£31,553 9 9	£27,904 15 4				

Nominal  
Value.

Market Value,  
31st December,  
1943.

Nature of Security.

#### ANDREW CARNEGIE RESEARCH FUND.

(Trustees : Sir Wm. Larke, K.B.E., James Henderson, The Hon. R. G. Lyttelton.)

£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
6,897	14	11	3½%	War Stock	...	...	...	...	...	...	...
1,800	0	0	Do.	...	...	...	...	...	...	...	...
2,693	12	0	3½%	Conversion Loan	...	...	...	...	...	...	...
2,642	12	0	3½%	Local Loans	...	...	...	...	...	...	...
2,250	0	0	North Eastern Electric Supply Company	3½%	Consolidated Debenture Stock	...	...	...	...	...	...
1,500	0	0	Great Western Railway	4%	Debenture Stock	...	...	...	...	...	...
2,000	0	0	London Midland & Scottish Railway	4%	Debenture Stock	...	...	...	...	...	...
1,312	0	0	London & North Eastern Railway	4%	1st Guaranteed Stock	...	...	...	...	...	...
5,000	0	0	Do.	4%	Debenture Stock	...	...	...	...	...	...
6,000	0	0	Do.	3½%	do.	...	...	...	...	...	...
2,250	0	0	3% Savings Bonds 1955/65	...	...	...	...	...	...	...	...
2,813	2	7	2½%	Consolidated Stock	...	...	...	...	...	...	...

£	s.	d.
£35,159	15	0

£	s.	d.
£29,938	0	5

#### WILLIAMS PRIZE FUND.

(Trustees : Sir Wm. Larke, K.B.E., James Henderson, The Hon. R. G. Lyttelton.)

£	s.	d.	£	s.	d.	£	s.	d.	
3,452	15	7	3½%	Conversion Loan	...	...	...	...	...

£	s.	d.
3,616	15	9

£	s.	d.
£418	0	0

(Signed) R. LYTTELTON.  
*Hon. Treasurer.*

#### BESSEMER MEDAL FUND.

(Trustees : Lord Airedale and Sir Francis Samuelson.)

£	s.	d.
400	0	0

£	s.	d.
2,670	0	0

(Signed) K. HEADLAM-MORLEY.  
*Secretary.*

We have examined the foregoing Balance Sheets and Income and Expenditure Accounts with the Books and Vouchers of the Institute and certify them to be correct. We have also verified the Balances at the Bankers and the Securities for the Investments shown above.

224 REGENT STREET,  
LONDON, W.1.  
15th March, 1944.

(Signed) W. B. KEEN & Co.  
*Chartered Accountants.*

## PRESIDENTIAL ADDRESS.

BY ARTHUR DORMAN.

SIR JOHN CRAIG, in his Presidential Address in 1940, said that he was only the second Scotsman to occupy this high office since the inception of The Iron and Steel Institute in 1869. On looking through the list of the distinguished men who have held this office I see that no fewer than twelve have come from the North-East Coast, so that it does appear that an injustice has been done to our friends across the border, a state of affairs which I hope will be rectified in the future. I appreciate, however, the honour conferred upon me.

As you know, the North-East Coast, owing chiefly to the discovery of the Cleveland ironstone main seam by Bolckow Vaughan & Co. in 1850, rapidly took the leading place in the manufacture of foundry and forge pig iron, and later on became one of the largest steel manufacturing districts in Great Britain. It has often been said that it is profitable to look back on the past to enable one to learn from experience useful lessons for the future, so I propose to give a short review of the development in the North-East district since the beginning of the century. The chief features have been the very large reduction in the demand for foundry pig iron, the steady development of the basic open-hearth process for the manufacture of steel, and a marked reduction in the number of blast-furnaces built, coupled with greater output per furnace and the erection of coke-ovens at the blast-furnaces. As a result of this the name "Ironmaster" has almost disappeared, together with practically all the old ironmaking firms—most of them household names—and this century has seen the gradual evolution of the large composite iron and steel works.

Although I do not intend to dwell on the distant past I find there were in 1880 no fewer than 167 blast-furnaces on the North-East Coast capable of being put into operation, whereas in 1900 there were only 123; the average number blowing during that year was 93—about 50 on Cleveland iron and the remainder on hematite and special iron—the average weekly make per furnace being just over 600 tons. The output of iron of the United Kingdom in 1900 was approximately 9,000,000 tons, the North-East Coast accounting for rather more than one-third of the total. The national steel output in 1900 was 4,900,000 tons, of which only about 300,000 tons were made by the basic open-hearth process and 490,000 tons in the basic Bessemer converter, the remainder being acid steel. The world production of pig iron was just under 40,000,000 tons and that of steel just under 28,000,000 tons.

It is interesting to compare the above figures with those for 1937, the last year for which complete published records are available, and during which the whole of the country produced 8,490,000 tons of pig iron. There were only 50 blast-furnaces on the North-East Coast, and the average number blowing during the year was 34; the total make of iron for the district was 2,429,000 tons, and the average weekly make per furnace had risen to 1,400 tons. This is a very small output compared with that of the large blast-furnaces in the United States of America and other parts of the world, but undoubtedly the use of a large proportion of lean local ironstone coupled with the long established practice of calcining it in kilns adjacent to the furnace has retarded the development of large blast-furnaces in this district.

The year 1937 saw the record make of steel ingots for the country to that date, the total being just under 13,000,000 tons, of which no less than 9,660,000 tons were produced by the basic open-hearth process. The production of basic Bessemer steel ingots over the year was 417,000 tons, but no steel had been produced by this process between 1924 and 1934. You will therefore see that 74% of the total ingots were made by the basic open-hearth process as against 6% made by this process in 1900. The world production of pig iron in 1937 was 102,000,000 tons and that of steel was 133,000,000 tons, so that the steel production of the world has definitely overtaken the iron production.

My object in quoting these figures is to show the large increase in the output of steel since the beginning of the century, especially by the basic open-hearth process, the small but steady decline in the production of iron in this country and the quite considerable reduction in the number of blast-furnaces in operation coupled with larger makes.

You will realise that it was not very easy to base large composite iron and steel works on the old blast-furnace plants. Our grandfathers were great pioneers and took full advantage of the cheap fuel, cheap local ironstone and the large demand for pig iron which existed in those days. Blast-furnaces were scattered up and down the country, in several parts of the County Durham and even in the Esk Valley near Whitby. Steel was still in its infancy. Although the British steel output had risen from about 2,000,000 tons a year in the early 'eighties, it was still short of 5,000,000 tons in 1900. Men such as my father, Sir Arthur Dorman, who showed great determination in encouraging the use of molten Cleveland iron in the manufacture of basic open-hearth steel, Mr. Benjamin Talbot, the inventor of the well-known process which bears his name, and Sir Hugh Bell—the last two being Past-Presidents of this Institute—saw clearly the necessity for the installation of large composite iron and steel works equipped with coke-ovens so as to get the full benefit of both coke-oven and blast-furnace gases in the steelworks.

Considerable progress was made in the first fourteen years of the century, but times were hard, competition from abroad was severe, and the cost of new plant and machinery was considerably greater than was necessary a generation earlier. The first world war found our industry inadequately equipped for the demands made on it, and as a consequence large schemes were undertaken during the war to meet the situation by building complete new steelworks. The financial arrangements which permitted these new works to be built were not generous, and, as some of the schemes were not completed till long after hostilities had ceased, several firms were left with unbalanced plants.

I do not propose to dwell on the post-war depression which fell in all its severity on our trade, but in 1933 the horizon cleared, orders became more plentiful and prospects more stable. As a result a number of blast-furnaces were modernised, new coke-ovens built and many improvements made in steel furnaces and rolling mills. In 1939 it is true to say that many of the steel furnace plants and rolling mills compared favourably with the best practice in any country, and, although there were still too many small blast-furnaces operating on the North-East Coast and in the country generally, a definite start had been made towards modernisation; in most cases modern coke-ovens were operating alongside the blast-furnaces and full advantage was taken of the coke-oven and blast-furnace gases.

I am not allowed, of course, to make any comment about the efforts that the trade has made during the present war, but I can say without fear of contradiction that it was much better equipped to meet this great emergency than it had been in 1914.

When one turns to the future several interesting questions arise, in all of which scientific research will play an important part. It seems certain that there will be an increased cost of fuel as a permanent feature operating in the future. To work the large modern blast-furnace satisfactorily careful preparation of all materials used is necessary, and beneficiation of the iron ores, especially those of the leaner kind, becomes increasingly important and economic the higher the level of coke prices. No doubt a great deal has been done, but it seems that attention might be given to the possibility of applying some form of magnetic roasting to certain of our lean home ores, to be followed by crushing, magnetic separation and finally sintering or agglomeration to a form suitable physically for large fast-driving furnaces.

It seems that such investigation is required, because all the home ores available in bulk are on the lean side and likely to get leaner. With both railway carriage and fuel likely to show much higher costs and with large quantities of lean home ores available I think the position would quickly become clear that a good deal of money could be expended in experiments upon the general lines suggested,

and, looking far ahead, the future of the iron trade in this country may hinge on whether such a result can be achieved or not at a reasonable cost. In any case, considerable quantities of foreign ores will be necessary if the present outputs are to be maintained or increased. It is generally accepted that attainment of optimum results in large modern furnaces demands a comprehensive scheme of crushing, grading and sintering of ores, and the charging of all ingoing materials according to size.

Another point which merits more scientific investigation than has been given to it in Britain is the consideration whether some benefits may not arise from enriching the air blown into the blast-furnace with a certain limited amount of oxygen. Although the cost of oxygen has in the past been very high, the probable development and extended use of synthetic products requiring nitrogen may enable this cost to fall to economic levels. The idea of using a limited amount of oxygen in the ordinary air blown has always been attractive, because by a slight variation in the amount added the blast-furnace operator would have better control of the quality of the products and secure more regular working. By replacing 20% of the ordinary air by oxygen the blast-furnace gases now running, say, 100 B.Th.U. per cu. ft. would be, although less in quantity, of much higher value, say, about 130 B.Th.U. per cu. ft. The matter certainly seems more feasible with the advance in the cost of fuel, and I believe experiments on these lines have been made in Belgium and Russia. Similarly, the use of dry blast, or, to be more exact, blast of controlled moisture content, becomes more attractive as fuel prices rise, and may prove economically possible even in this country, now that modern systems of refrigeration have overcome many of the disabilities of the earlier methods of drying the blast.

In my opinion the 1937 output of iron on the North-East Coast could have been more economically made in 15 large blast-furnaces instead of the 34 which were then blowing, and the average weekly make per furnace should be 3,000 tons at least, or considerably more if adequate supplies of rich foreign ores were available or some such scheme as that mentioned previously of treating the lean home ores became practicable.

The future of the steel furnace is a very interesting question. Will the basic Bessemer process come back again into general favour? Modern supporters maintain that the exclusion of basic Bessemer steel from most British Standard Specifications arose from its unreliability during the early days of the process and that engineers are prejudiced in refusing to recognise improvements which have been made in recent installations. Undoubtedly progress can be claimed as the result of experience, and the steel now made is entirely suitable for many purposes, but one cannot altogether ignore the contrast between the rapid reactions of the Bessemer blow and the careful control of slag and metal during the

working of an open-hearth charge. Specifications in the future are likely to become more exacting.

A further strong point in favour of the open-hearth process is its ability to consume varying quantities of scrap and thus take advantage of market conditions. It is very probable that considerable quantities of scrap will be available after the war, and I think every large steelworks should install a scrap preparation plant, so that the scrap may be charged into the furnace in suitable lengths or in bundles of a handy size.

When the largest possible steel output is required I think large fixed open-hearth steel furnaces will come into favour and that their size may be increased up to, say, 120 tons for cold-charged units and 200 tons or even more in the case of furnaces using a high proportion of hot metal. When using high-phosphorus hot metal produced largely from our Jurassic ironstones, the large tilting furnace of, say, 300 tons capacity has strong claims, and will continue to have its advocates. Active mixers, too, may tend to become larger, up to, say, 1,000 tons capacity.

I am convinced that with proper care and skill really high-grade steel can be made under these conditions, but there will no doubt be an increasing demand for special carbon and alloy steels. Therefore, I think many steel furnace plants will have a few smaller furnaces installed for this purpose.

At the present time it would appear that the cost of electrical energy will preclude, in this country at least, the use of the electric furnace for the ordinary run of steel. However, it will be interesting to see whether future developments in the field of power generation will enable the cost of electric steel to be reduced, since it has many advantages for certain special purposes. One hears of electric furnaces of as much as 70 tons capacity in the United States of America, and ingenious charging devices facilitating high rates of output are now the order of the day.

With iron and steel being made in many new countries during the last ten or twenty years, I feel very strongly that it is essential that the finishing trades of this country should have as a base a highly efficient heavy iron and steel industry capable of producing an adequate output of iron and steel under most modern conditions. We must regain and expand our export trade, which will only be possible if all sections of the industry are equipped to meet world competition. I consider that there is no reason why the 1937 output of steel should not be exceeded. This will necessitate a great deal of reconstruction, as the war conditions which have now lasted nearly five years have of necessity deferred many schemes of modernisation. It is important that a commencement of this work be made at the earliest possible moment, and also that immediate steps be taken to overtake the arrears of repairs and maintenance which inevitably have accumulated through working at high pressure during the period of the war.

Although I have refrained from commenting on the finishing processes, yet I hope I have said enough to show the necessity for research.

A very interesting review of the Joint Research Committees of The Iron and Steel Institute and the British Iron and Steel Federation<sup>1</sup> has recently been published, which shows clearly the excellent work that has been done for a number of years. Sir William Larke, the Chairman of the Iron and Steel Industrial Research Council, has been largely instrumental in centralising the efforts of the trade, and our thanks are due to him.

The Research Council has had a grant from the Department of Scientific and Industrial Research and from the trade, but it does not maintain a Central Research Station or laboratory. Many investigations have been carried out at various works and laboratories of the industry, and the late Dr. W. H. Hatfield, Chairman of many of the Joint Committees of the Federation and the Institute, was always an enthusiastic supporter of research. A lot of research was done by many firms in the industry which never came before the Research Council. I have in mind the numerous experiments on steel, rivets and wire rope which were made in connection with the Sydney Harbour Bridge contract, and the 1,250-ton testing machine which was installed to make the necessary tests for this contract. But more research is demanded, and it is felt that these joint efforts should be merged and all co-operative research should be administered by one organisation, so that there should be no division of responsibility. This has resulted in the formation of the Iron and Steel Research Association, which will be financed by the British Iron and Steel Federation and the Department of Scientific and Industrial Research and will be under the control of a Council on which The Iron and Steel Institute will be represented. It is intended to appoint a full-time Director of Research and possibly in due course to have a Central Laboratory, though it is hoped that there will be no curtailment of extra-mural activities.

The Iron and Steel Institute has a great opportunity here to help this new Research Association and research generally. It is hoped that the Institute's building and the extensive joint library of the Institute and the Institute of Metals will be at the disposal of the Association and that the Institute will undertake the publication of papers and reports issued by the Association.

I trust that it may be possible for the Institute to help in bringing about a scheme of affiliation with the local Technical Institutes, so that joint meetings may be held several times a year in the various districts and encouragement given to the younger members of the staffs of the iron and steel companies to join their local Associations for a small subscription, and, should they wish, The Iron and Steel Institute on payment of a further reasonable sum.

<sup>1</sup> *The Iron and Steel Institute, 1943, Special Report No. 29.*

I look forward to foremen and workmen joining these local bodies, and clearly the more members we can get the cheaper will be the subscription. One or two of these local Institutes are as old as or older than the Institute itself and naturally wish to maintain their autonomy, but I am sure that the Institute and the local bodies will all benefit should we succeed jointly in bringing into being a scheme of affiliation which will stimulate our members and increase the enthusiasm of young students.

The proposed new scheme for National Certificates in Metallurgy, which we hope will be in operation in a few months' time, should also prove of very real value to these young students.

It will enable those who attend Technical Colleges to obtain a nationally recognised award as a result of their successful endeavours. We need more young men with scientific and technical training in our works, and we want to help those who are already engaged in the industry to get this training. National Certificates will be one means of showing that they are properly qualified.

Doubtless, arrangements will also shortly be made for metallurgists by which those who have proper qualifications, National Certificates among them, will be able to graduate to professional membership.

Personally I think this most desirable. It would result in metallurgy taking its rightful place as a profession alongside chemistry, engineering and physics.

In view of the importance of the industry's dependence on metallurgy, I am bound to say that I think that all steps should be welcomed which tend to encourage the study of the subject and which will raise the prestige of the profession. Our Institute can give valuable help.

# SOME NOTES ON SLAGS AND SLAG CONTROL IN BASIC OPEN-HEARTH TILTING FURNACES USING PHOSPHORIC IRON.<sup>1</sup>

BY A. JACKSON (APPLEBY-FRODINGHAM STEEL CO., LTD., SCUNTHORPE).

## SUMMARY.

The notes illustrate the chronological development of a slag control method, designed first for use during refining, but subsequently enlarged to embody also the charging of lime in furnaces using high percentages of molten phosphoric iron.

Commencing with a brief general résumé of the process, the paper shows the variable nature of the iron used and a series of tapping-slag analyses, illustrating a ratio between the total slag iron and the slag acids, silica plus phosphoric acid. From this follows the development of slag control for refining. Next the method of estimating and adding the limestone for charging is described, followed by three series of slag analyses taken just before removing the primary slag, from the primary slag and from the slag during tapping. The relationship between the slag and metal composition is indicated and graphs are plotted. It is also shown that the slag iron varies throughout refining with the iron in the primary slag before removal, which effect, though somewhat reduced towards tapping, is still appreciable. These slag irons vary within limits with the silicon in the mixer iron charged, and tend to support the previous impression that changes in the composition of the blast-furnace iron are reflected in the properties of the finished steel.

The mean analyses of a large number of slags are presented, from which numerous relationships can be developed, the most interesting probably being the inverse type of ratio between the silica plus phosphoric acid and the total iron, or iron oxides, with relatively constant lime. This tends to suggest that iron oxides may replace silica and phosphoric acid in the silico-phosphates of lime normally present in slags of this type, or that they associate in relatively definite quantities with any lime present which is not in combination with silica and phosphoric acid.

The conclusions point to some increased production resulting from the application of the methods outlined, but in particular indicate slag control to be one more step towards attaining uniformity of operation and product in the basic open-hearth. The developments used for the manufacture of other than ordinary boiler plate and section steels are not described in these notes.

## *Résumé of the Steelmaking Operation.*

THE steelmaking operation to which the subsequent notes refer is conducted in tilting furnaces of up to 300 tons capacity and using 70–80% of molten phosphoric pig iron. At tapping no slag is removed from the furnace, so that on completion the hearth will contain the whole of the refining slag and from 20 to 60 tons of finished steel. To this slag are added the limestone and oxide con-

<sup>1</sup> Received December 13, 1943.

sidered necessary for the following charge, followed by the scrap and molten metal. When these are completely melted, the bath composition has been adjusted as necessary and a good heat obtained, the slag is removed as completely as possible by tilting the furnace. This is termed the "slag-off" or primary slag, and normally 1-2 in. of slag remain in the hearth at this time. Further additions of limestone, oxide and molten mixer metal are added as required, and, when melted, form the "refining slag." When the furnace taps, from two to four ladles are taken out in quick succession, and a slag sample is taken between the first and second ladle; this is termed the "tapping slag." The time from slag-off to tapping the first ladle is the "refining time." For various reasons, metallurgical and otherwise, further additions of molten mixer iron, along with suitable quantities of oxide and flux, may be made during refining. The tons of metal added are divided by the mean tons per hour produced throughout the charge, and this number of hours, when deducted from the refining time, gives the "net refining time." The addition of this "extra metal" during refining reduces the net refining time, presumably because of the rapid rate of solution of lime or limestone at this period of the operation.

#### *Variation of Blast-Furnace Iron Composition.*

In this process of steelmaking the high percentage of iron used can cause considerable operational variations, both in output rate and in steel quality, should the analysis vary within what may appear to be very small limits when expressed as percentages. Variations in iron composition are damped out considerably in the semi-active types of mixer used, but they cannot be evened out completely unless the mixers are not worked to the limit of their activity for those periods when the incoming iron impurity is lower than average. To maintain maximum efficiency the mixers should be worked to the full. This will not damp out the normal fluctuations of composition of the blast-furnace iron, but will reduce their amplitude. The effects of the variations in the iron from the mixer on the steel furnaces can then be further reduced by judicious adjustment of the fluxes and oxides charged therein. These effects subsequently show up in the slag composition and thus come under the general heading of "slag control." Developments have taken place under this head over several years, and in the subsequent discussion the points are discussed chronologically. This line is taken in preference to an endeavour to paint a more logical picture, as obviously still further work on slags and their control remains to be done.

The average analyses of the iron used for the last four six-monthly periods to June, 1943, are shown in Table I. In the first two half-yearly samples only fluxes and oxides were added to the mixers; in the latter two, however, 1.20 and 2.03 cwt. of scrap per ton of iron, respectively, were added in addition. The reduction in phosphorus is quite appreciable in the latter examples.

TABLE I.—*Average Mixer-Iron Composition.*

Four six-monthly periods to June, 1943.

Iron into Mixer.				Iron from Mixer.			
P. %.	Mn. %.	Si. %.	S. %.	P. %.	Mn. %.	Si. %.	S. %.
1.60	1.14	0.79	0.083	1.41	0.63	0.29	0.064
1.54	1.00	0.83	0.087	1.40	0.61	0.29	0.067
1.52	1.00	0.75	0.087	1.31	0.63	0.26	0.069
1.49	0.94	0.84	0.089	1.19	0.59	0.29	0.069

The figures in Table I., whilst giving the average analysis of the molten iron used, do not show the daily or hourly variations that can occur owing to changes in the blast-furnace-iron analysis, varying steel plant demand, gas shortages, &c. These variations are

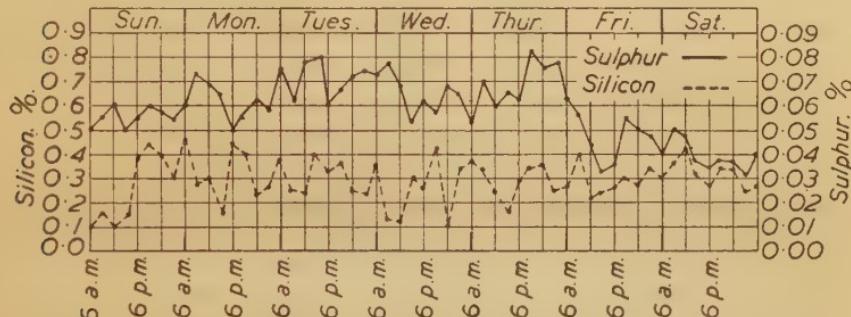


FIG. 1.—Sulphur and Silicon Variations in a Normal Week's Working.

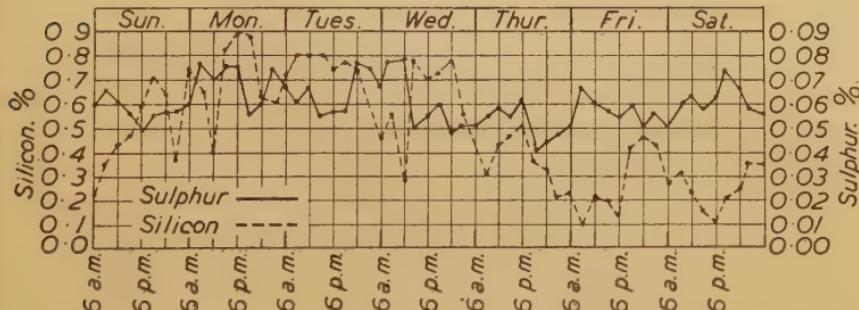


FIG. 2.—Sulphur and Silicon Variations in a Bad Week's Working.

illustrated in a normal and bad week in Figs. 1 and 2, which are traced from the charts normally used for plotting blast-furnace- and mixer-iron analyses. Many efforts have been made from time to time to overcome this difficulty of variable iron composition from the mixers. A method giving some success is outlined later.

For many years it has been felt that iron quality and steel quality are directly related; some evidence is also put forward which tends to indicate that this is a possibility.

### *Tapping Slags.*

Several years ago, in an effort to obtain more knowledge of the composition of furnace slags, a series of tapping slags was obtained, grouped according to total-iron content, and analysed. The results are shown in Table II. These slags, which were all taken during

TABLE II.—*Tapping-Slag Analyses (Group 3).*

No. of Samples.	SiO <sub>2</sub> . %.	Mn. %.	CaO. %.	P <sub>2</sub> O <sub>5</sub> . %.	Total Fe. %.	P <sub>2</sub> O <sub>5</sub> + SiO <sub>2</sub> . %.
100	8.40	4.75	47.1	14.43	10.8	22.83
51	7.80	4.99	47.4	14.81	10.9	22.61
71	8.05	4.84	47.6	14.50	11.1	22.55
139	8.35	4.96	47.9	14.58	11.4	22.93
111	8.50	5.01	47.4	13.96	11.8	22.96
52	7.45	4.94	47.3	14.27	12.0	21.72
87	7.90	5.09	47.3	13.50	12.3	21.40
80	7.25	5.38	46.2	12.42	14.1	19.67

actual tapping, represented as nearly uniform conditions as it was possible to obtain, *i.e.*, the bath contained less than 0.06% of phosphorus, with a normal tapping heat and good slag condition. Whilst interesting, these slags showed no outstanding relationships until that between total iron and SiO<sub>2</sub> + P<sub>2</sub>O<sub>5</sub> was noticed; this gave a reasonably straight-line plot. A further series of similar magnitude taken later confirmed this relationship.

At this point the author became aware of the slag-control method just being commenced at the works of Messrs. Steel, Peech and Tozer. In this method slag and metal analyses, including SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>, were made when the furnace was almost melted. From the results the requisite additions were made to the bath to enable, amongst other things, the slag to finish at a predetermined figure for total P<sub>2</sub>O<sub>5</sub> + SiO<sub>2</sub>, depending upon the class of steel to be made. The methods adopted and calculations made were very generously explained by Mr. N. H. Bacon, Mr. J. T. Brooke and Mr. D. Manterfield. It was immediately obvious that the method outlined could be more easily applied to a tilting furnace than to a fixed one, because in the former case most of the slag is removed when the charge is melted, so that, by assuming a constant quantity and analysis for the little slag remaining, one could calculate quite well the finishings required in refining from the analysis and weight of steel in the furnace at this point. No slag analysis was really necessary; thus, the time for making the requisite additions was confined to that necessary to do the routine bath analyses for phosphorus

and carbon. These assumptions, which were modified later, formed the primary basis for slag control during refining.

### Slag Control.

From various slag analyses taken over considerable periods, it appears that the acids  $\text{SiO}_2$  and  $\text{P}_2\text{O}_5$  can replace each other over the ranges normally found in the slags from the Appleby furnaces, without material alteration in the composition of the remainder of the slag.

Table II. shows a series of tapping slags from furnaces making plain carbon steels of 0·08–0·20% carbon. It also shows that normal commercial steels can be made with a total  $\text{P}_2\text{O}_5 + \text{SiO}_2$  content of 23% without danger of rephosphorisation with a slag iron figure of 11%, and that about 47% of  $\text{CaO}$  is to be expected in the slag.

For purposes of calculation for the finishing slag composition a ratio of  $\text{SiO}_2 + \text{P}_2\text{O}_5$  to  $\text{CaO}$  of 23 : 47 was adopted.

The materials used had compositions as follows :

	Limestone.				Lime.
Moisture. %	.	:	:	7·0	...
$\text{SiO}_2$ . %	:	:	:	1·1	2·5
$\text{CaO}$ . %	:	:	:	51·1	92·5
$\text{MgO}$ . %	:	:	:	0·4	0·7
Loss on ignition. %	:	:	:	40·0	2·3

After deduction for silica and addition for magnesia, in view of variations in the moisture, &c., a figure of 50% was taken for the available lime in the limestone.

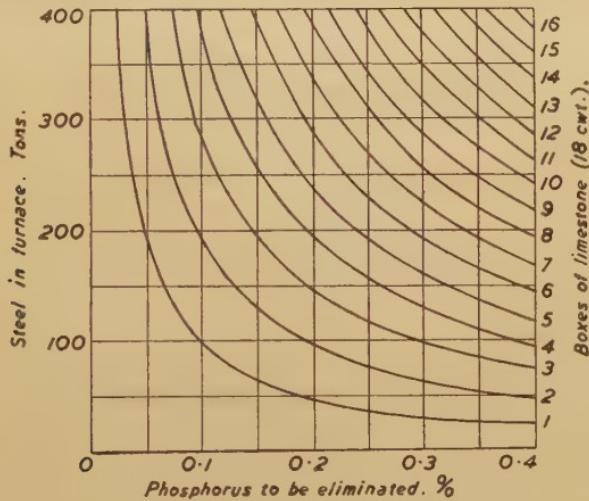


FIG. 3.—Limestone Additions Required for Various Bath Compositions and Weights.

From these figures calculations were made showing the limestone required for various bath compositions and weights. From these, Fig. 3 was produced and put into use, all additions being made

accordingly. The limestone is added in one lot immediately after "slag-off," and the additions are based on a metal sample taken from the bath half-an-hour before "slagging-off" is completed. This allows time for the sample to be analysed by the laboratory, and the results are available by the time that slagging is finished. Formerly, all additions were made on samples taken immediately after slag-off, and some time was therefore lost in waiting for the analytical results. Numerous tests showed that the sample taken a few minutes before slagging commenced was for all practical purposes sufficiently accurate to enable the additions necessary to form a new slag to be calculated.

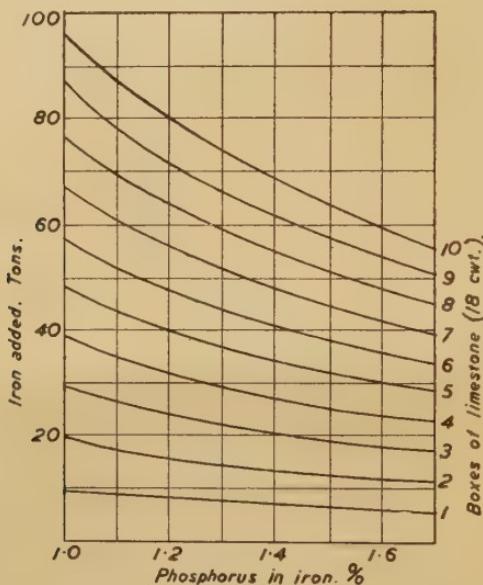


FIG. 4.—Limestone Additions to Finishing Slag in relation to the phosphorus content and weight of the mixer iron added.

During refining, the bath carbon content is almost invariably adjusted by the addition of quantities of mixer metal. The curves in Figs. 4 and 5 were prepared and used for calculating the limestone additions for varying quantities of this "extra metal" added.

Oxide additions in any appreciable quantity are seldom necessary during refining. It was found that the slag oxidation from carbon dioxide and moisture in the limestone, which was always used until refining was complete, plus flame oxidation, were normally sufficient for the removal of all phosphorus. A useful guide for oxide additions was to reduce the metal additions to terms of carbon, roughly 10 tons raising the bath carbon content by 0.10%. This figure was

added to the carbon already in the bath and an allowance of one box (30 cwt.) of scale made for every 0·10% of carbon that it was desired to remove before refining was complete. This method of operation worked in general with surprising accuracy and reduced the average net refining time by about 30 min. from a figure of 135 min. It was found, however, that occasionally the phosphorus failed to drop to the tapping specification without further limestone or oxide additions. It soon became evident that this was liable to occur when the iron in the slag-off slag was low—say, under 7%. In about half of these instances extra oxide would raise the iron, but sometimes, no matter how much was added, the slag iron stayed down, and the furnace was again slagged and a third slag made. This corrected

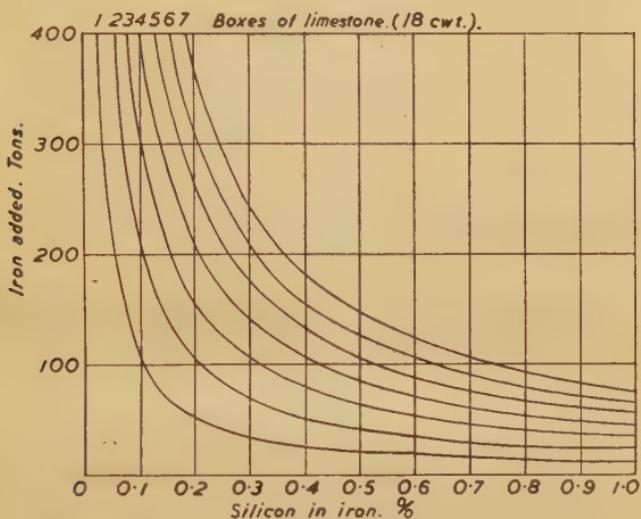


FIG. 5.—Limestone Additions to Finishing Slag in relation to the silicon content and weight of mixer iron added.

the trouble at once. Further analyses showed that this trouble was due to the slag left in the furnace after slagging being unduly rich in acids, and also possibly to the quantity left in the furnace being a little above the normal. Slag analyses indicated that the acids are related to the slag iron; therefore a scale of varying limestone for the normal ranges of slag iron was produced, and a slag sample was taken with the opening metal sample and analysed for total iron on each charge. This corrected the trouble at once, and little or no extra oxide was necessary under these circumstances. The net refining time with these low-iron slags, however, increased, as was to be expected. A series of results taken over a period of about three months is recorded in Fig. 6.

Table III. gives typical quantities for the extra limestone necessary to compensate for the extra acidity in the primary slag as

indicated by the slag-off iron figure. In using this Table, the limestone necessary to refine the charge is calculated from the bath

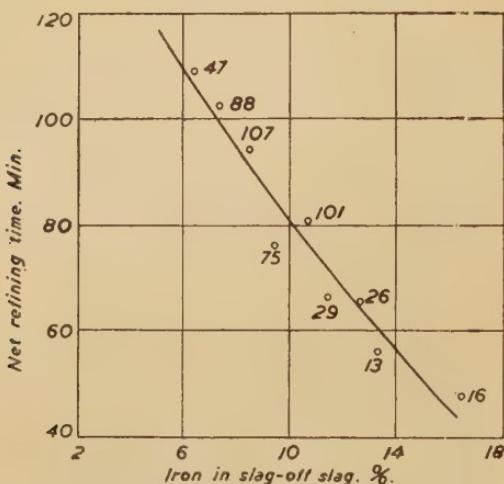


FIG. 6.—Statistical Analysis of the Iron in the "Slag-off" Slag in Relation to the Net Refining Time.

TABLE III.—*Typical Limestone Additions to Compensate for Extra Acidity in Primary Slag.*

Iron in Primary Slag. %	Slag Weight in Furnace—	
	5 tons.	10 tons.
6	2 boxes limestone.	4½ boxes limestone.
8	1½ ", "	3 ", "
10	½ box ", "	1 box ", "
12	Nil	Nil
14	-1 ", "	-2 boxes "

composition and extra mixer metal to be used, if any. This figure is then modified by the amount stated, according to the total iron in the primary slag. It will be noted that limestone is deducted for high iron contents. In actual practice, of course, further molten iron would be necessary in these cases to reduce the state of oxidation of the bath.

#### *Calculations for Charging.*

Shortly after the commencement of slag control for refining, calculations were made to estimate the quantity of fluxes required with the original charge. For this it was decided to aim for a primary slag composition containing 26% of  $P_2O_5 + SiO_2$ , and Figs. 7 and 8

were used to calculate the charge compositions, based on the expected composition of the iron from the mixer. This was judged from the trends of the three-hourly plots of iron analyses from the mixers and the cast analyses from the blast-furnaces.

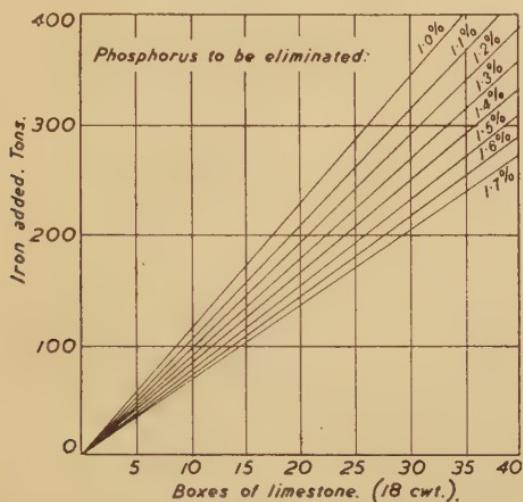


FIG. 7.—Limestone Additions to Primary Slag to give  $P_2O_5 + SiO_2 = 26\%$  in relation to the phosphorus to be eliminated.

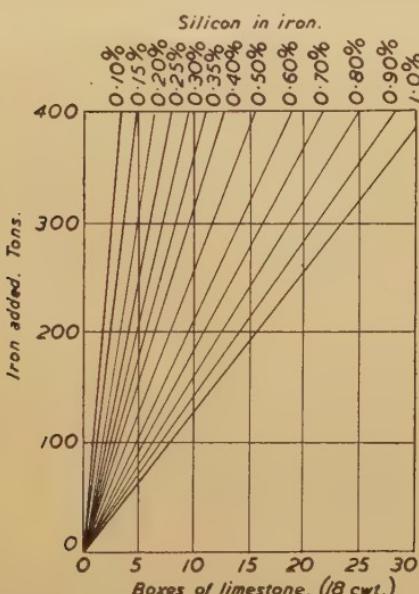


FIG. 8.—Limestone Additions to Primary Slag to give  $P_2O_5 + SiO_2 = 26\%$  in relation to the silicon content of the iron.

After some weeks, this method was modified as follows :

(1) The limestone for the whole charge was calculated to cover all requirements except the silicon in the iron from the mixer (*see Appendix I.*).

(2) Charging proceeded normally until the molten iron was charged. Only about 80% of the total iron was added at this point, a sample of which was sent to the laboratory.

(3) Two to four hours later, based on the above sample, the limestone necessary for the silicon in the whole charge was calculated and added.

(4) The remainder of the mixer metal was added to complete the charge.

By these means, a very close approximation to the actual limestone requirement can be obtained, even should the silicon in the mixer iron vary within reasonable limits from the expected analysis. If the furnace melts hard,<sup>1</sup> owing to a high silicon content after the charging is finished, oxides can easily be added to rectify this just before the charge melts, and with much less delay to the process than if the furnace had also been short of lime.

This method gave improved control of the melting sample and greater uniformity of conditions at the start of refining.

A further small modification followed shortly to compensate for excess lime added during refining. This excess lime resulted from the necessity to add burnt lime to the furnace while awaiting the final tapping analysis and during tapping. At this stage of furnace operation, lime goes into the slag very much more quickly than during melting; in consequence, opportunity is taken to add lime in the late stages of the process, some being added between ladles while tapping and a further few boxes to the slag immediately after tapping. Rephosphorisation seldom occurs, and the melting rate of the following charge is accelerated, as less limestone need be added with the charge, whilst that added at the end of refining and at tapping is already largely in solution in the slag.

During the time that slag control was in use, a large number of samples were obtained. For each charge, three slags were taken at sharply defined and critical points, as follows :

(1) About 30 min. before removing the slag (*i.e.*, the furnace was not quite clear melted).

(2) During removal of the primary slag-off slag (the furnace being well melted at this stage).

(3) During tapping (normally between the first and second ladle).

These slags were grouped according to their iron contents and analysed. The analyses are recorded in Tables IV., V. and VI., and

<sup>1</sup> That is, with a high carbon content.

TABLE IV.—*Slag 30 Min. before "Slag-off."*

No. of Samples.	SiO <sub>2</sub> . %.	CaO. %.	P <sub>2</sub> O <sub>5</sub> . %.	Mn. %.	FeO. %.	Fe <sub>2</sub> O <sub>3</sub> . %.	Total Fe. %.	SiO <sub>2</sub> + P <sub>2</sub> O <sub>5</sub> . %.
<i>Group 1.</i>								
100	12.00	46.7	18.75	...	3.60	4.57	6.0	30.75
246	11.5	46.4	18.25	...	4.13	4.86	6.6	29.75
269	10.4	47.0	18.59	...	4.77	5.14	7.3	28.99
184	10.2	47.2	17.20	...	5.27	6.43	8.6	27.40
115	10.3	46.4	17.59	...	5.66	6.00	8.6	27.89
71	9.9	46.6	16.82	...	5.66	7.14	9.4	26.72
53	9.3	47.0	16.28	...	6.95	6.86	10.2	25.58
25	8.4	44.2	14.74	...	8.74	8.71	12.9	23.14
<i>Group 2.</i>								
353	10.5	47.4	18.21	3.85	4.24	4.73	6.6	28.71
379	9.9	47.6	17.82	3.69	4.89	5.83	7.9	27.72
363	9.5	46.6	17.36	3.86	5.40	6.43	8.7	26.86
214	9.5	45.6	16.43	3.76	6.30	6.00	9.1	25.93
104	9.0	45.4	16.05	3.76	6.56	7.43	10.3	25.05
84	7.8	45.4	14.74	3.74	8.74	7.71	12.2	22.54
55	7.7	44.6	14.27	3.47	9.90	9.57	14.4	21.97

TABLE V.—*Primary ("Slag-off") Slag.*

No. of Samples.	SiO <sub>2</sub> . %.	CaO. %.	P <sub>2</sub> O <sub>5</sub> . %.	Mn. %.	FeO. %.	Fe <sub>2</sub> O <sub>3</sub> . %.	Total Fe. %.	SiO <sub>2</sub> + P <sub>2</sub> O <sub>5</sub> . %.
<i>Group 1.</i>								
67	12.70	47.2	18.59	...	3.21	4.29	5.60	31.29
135	11.00	47.0	17.74	...	4.50	5.14	7.10	28.74
155	11.10	47.4	18.44	...	4.51	5.71	7.50	29.54
135	10.50	48.2	17.13	...	4.89	5.86	7.90	27.63
145	10.10	48.4	17.28	...	5.79	6.29	8.90	27.38
117	8.60	47.8	17.28	...	5.94	7.43	9.90	25.88
147	8.46	47.5	16.36	...	7.20	6.95	10.40	24.82
62	8.20	46.8	14.50	...	8.23	8.71	12.50	22.70
<i>Group 2.</i>								
18	10.7	47.6	19.14	3.76	3.60	5.43	6.6	29.84
22	9.9	48.6	18.98	3.93	4.11	6.73	7.9	28.88
72	9.2	48.6	18.28	3.79	4.11	6.43	7.7	27.48
164	9.2	48.4	17.51	3.85	4.76	7.14	8.7	26.71
271	8.9	48.4	16.59	3.71	5.53	6.73	9.0	25.49
321	8.0	48.4	15.97	3.66	6.04	7.28	9.8	23.97
162	8.0	47.8	15.51	3.66	6.81	9.43	11.9	23.51
54	7.5	47.0	14.04	3.57	8.74	9.14	13.2	21.54

TABLE VI.—*Tapping Slags.*

No. of Samples.	SiO <sub>2</sub> , %.	CaO., %.	P <sub>2</sub> O <sub>5</sub> , %.	Mn., %.	FeO., %.	Fe <sub>2</sub> O <sub>3</sub> , %.	Total Fe., %.	SiO <sub>2</sub> + P <sub>2</sub> O <sub>5</sub> , %.
Group 1.								
68	10.50	47.8	17.05	...	5.14	5.57	7.90	27.55
66	9.10	49.2	15.97	...	6.04	6.71	9.40	25.07
100	9.10	48.0	15.58	...	6.69	7.29	10.30	24.68
113	8.70	48.8	14.74	...	7.33	6.86	10.50	23.44
75	8.50	48.0	15.04	...	7.46	8.14	11.50	23.54
37	8.20	48.6	13.27	...	8.23	9.00	12.70	21.47
30	7.50	46.6	12.81	...	10.54	9.59	12.80	20.31
Group 2.								
21	11.30	47.0	18.13	4.04	5.27	4.14	7.0	29.43
54	9.50	48.2	17.74	4.00	5.14	5.57	7.9	27.24
135	8.80	48.6	16.59	3.88	7.20	5.50	9.1	25.39
215	8.60	49.0	15.66	3.88	6.69	7.14	10.2	24.26
300	8.30	48.8	15.28	3.72	7.46	6.86	10.6	23.58
259	7.60	48.6	14.97	3.76	7.84	7.57	11.4	22.57
224	7.50	48.4	13.89	3.80	8.49	8.00	12.2	21.39
116	7.40	47.8	13.81	3.76	9.00	8.28	12.8	21.21
64	6.90	47.0	12.50	3.42	9.90	9.00	14.0	19.40
22	7.30	47.8	12.50	3.76	10.41	8.70	13.8	19.80
12	6.60	45.2	11.73	3.65	10.67	10.41	15.6	18.33
6	5.00	45.6	10.96	4.21	13.76	10.73	18.2	15.96

graphs showing the relationship between the total iron and the P<sub>2</sub>O<sub>5</sub> + SiO<sub>2</sub> in the slags are plotted in Figs. 9, 10 and 11. In each

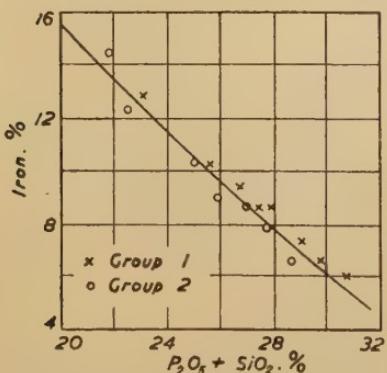


FIG. 9.—Relationship of P<sub>2</sub>O<sub>5</sub> + SiO<sub>2</sub> to Iron in Slag 30 min. before Melted.

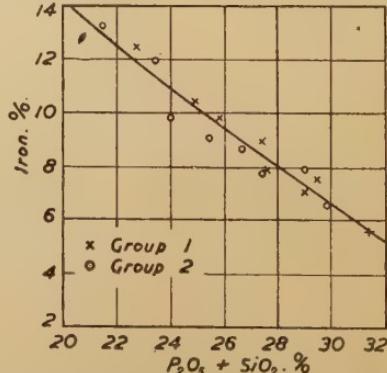


FIG. 10.—Relationship of P<sub>2</sub>O<sub>5</sub> + SiO<sub>2</sub> to Iron in Primary (Slag-off) Slag.

case the relationship appears to be quite close, and indicates that a very useful guide to the content of acids in a slag may be obtained directly from the total-iron figure, which can be accurately estimated in a very few minutes.

The results of the slag and metal samples taken about 30 min. before the furnace was fully clear melted and when it was on the boil indicated that little change in composition occurred during these last few minutes; therefore the slag-off samples were eventually discontinued, as the earlier sample was sufficiently accurate to permit of the correct refining additions being made to the furnace.

#### *Slag-Metal Relationships.*

To obtain information of the metal composition in conjunction with the various slags taken, numerous metal samples were also examined; the samples were as follows :

(1) Bath sample for carbon, phosphorus and sulphur with the first slag sample.

(2) Slag sample for iron when the refining slag was completely formed.

(3) Final bath sample for carbon, phosphorus and manganese just prior to tapping.

(4) Tapping slag for iron between the first and second ladle, and metal samples for the mean phosphorus contents of the first and second ladles.

These figures are tabulated in Table VII.; they confirm very closely the impressions conveyed from a smaller number of samples (476) tested previously.

TABLE VII.—*Slag and Metal Analyses.*

No. of Samples.	Sample taken 30 min. before Slag-off.				1st Slag Sample during Refining. Fe. %.	Bath Sample at Tapping.			Tapping Slag between 1st and 2nd Ladle.		Pit-Sample Phosphorus. %.		
	Slag. Fe. %.	Bath.				C. %.	P. %.	Mn. %.	1st Ladle. Fe. %.	2nd Ladle.	1st Ladle.	2nd Ladle.	
		C. %.	P. %.	S. %.		%.	%.	%.	%.	%.	%.	%.	
34	5.4	0.28	0.21	0.059	10.0	0.15	0.055	0.19	11.2	0.044	0.045		
122	6.5	0.23	0.16	0.060	10.3	0.16	0.048	0.20	11.6	0.044	0.046		
240	7.5	0.22	0.124	0.058	10.9	0.16	0.047	0.19	11.7	0.041	0.043		
322	8.6	0.20	0.099	0.057	11.6	0.17	0.042	0.18	12.0	0.040	0.042		
325	9.4	0.19	0.086	0.056	11.8	0.17	0.041	0.18	12.1	0.037	0.040		
252	10.4	0.18	0.078	0.056	12.3	0.18	0.040	0.17	12.5	0.037	0.039		
198	11.4	0.17	0.075	0.055	12.6	0.16	0.040	0.17	12.6	0.035	0.038		
126	12.2	0.15	0.065	0.055	13.6	0.16	0.035	0.16	12.9	0.033	0.035		
87	13.4	0.17	0.066	0.054	13.4	0.16	0.035	0.17	13.0	0.035	0.036		
111	16.0	0.13	0.065	0.055	14.2	0.16	0.032	0.16	13.3	0.034	0.036		

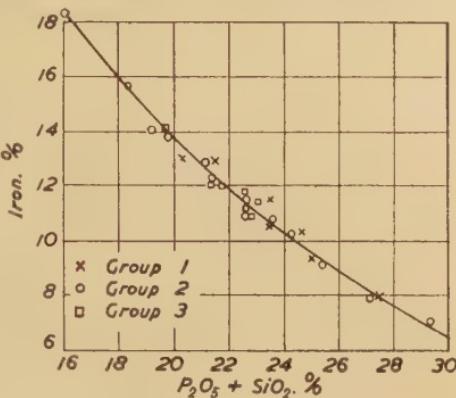


FIG. 11.—Relationship of  $P_2O_5 + SiO_2$  to Iron in Tapping Slag.

Figs. 12, 13 and 14 indicate the various relationships clearly, but the most striking point is the relationship between the iron at slag-

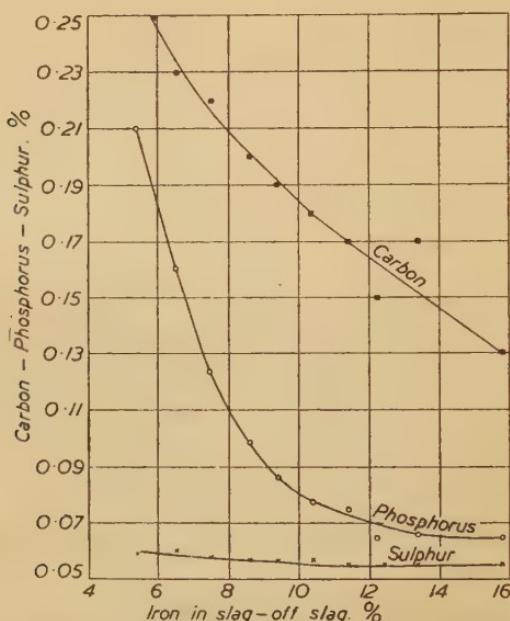


FIG. 12.—Relationship of Carbon, Phosphorus and Sulphur in Bath to Iron in Slag-off Slag.

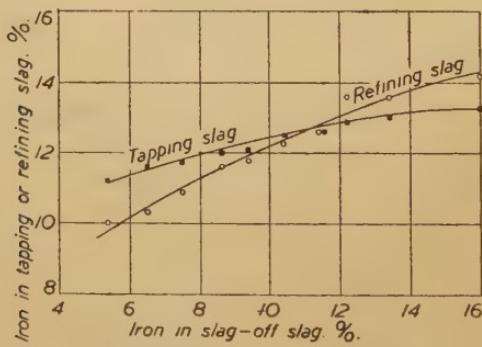


FIG. 13.—Relationship of Iron in Slag-off Slag to that in Refining Slag and Tapping Slag.

off and at tapping. This shows markedly that the two follow closely; similarly, it means that high iron at slagging gives high iron and its attendant effects at tapping.

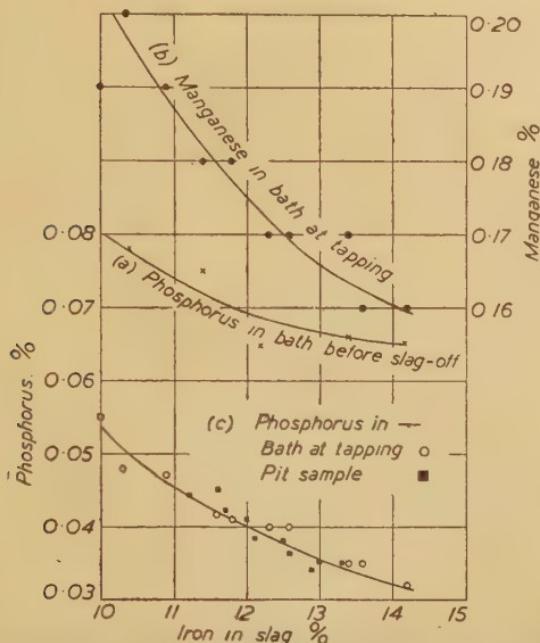


FIG. 14.—Relationship of Iron in Slag to (a) Phosphorus in Bath before Slag-off, (b) Manganese in Bath at Tapping, and (c) Phosphorus in Bath at Tapping and in Pit Sample.

#### Variation in Iron Analyses.

For many years we have felt that variations in the quality of the iron from the blast-furnaces affected the quality of the finished steel ingots. Many observations failed to give concrete evidence of this, however, but appeared to show that variations in the steel quality occurred while the blast-furnace iron was changing from one quality to the other, and then settled down again more or less uniformly as long as the iron remained of the new type.

From the graphs reproduced here it seems fairly certain that the factors which cause the iron content of the slag-off slag to vary above or below the mean will cause the refining and tapping slags to vary in a similar manner. This gives either a steel made under a high-oxide slag, requiring extra mixer iron for deoxidation before tapping, or a low slag iron content at slagging which will accompany a hard melt with its slower refining. Charges which melt hard often foam and thus further delay the process. If the blast-furnace iron remains constant at the new level, then either of these two conditions will be rectified in the subsequent charge by variations in the added oxide and limestone. The essential element affecting the variation in blast-furnace iron is, of course, silicon, with smaller variations due to other constituents.

Blast-furnace irregularities are now damped out in part by

mixer practice, and still further by charging control, but, in spite of this, the variations are still obviously of considerable importance, though the general regularity of working may be much improved.

In addition to the sudden swings in iron analysis, statistical analysis tends to show a fundamental relationship between the silicon in the mixer iron charged and the slag iron when the furnace is nearly melted. This is illustrated in Table VIII. This Table indi-

TABLE VIII.—*Mixer-Iron Silicon and Slag Iron Relationship.*

Furnace nearly melted.

No. of Samples.	Mixer Iron.				Slag Iron ( $\frac{1}{2}$ hr. before Slag-off). %.
	Si. %.	Mn. %.	S. %.	P. %.	
390	Under 0·2	0·48	0·075	1·25	10·1
756	0·20-0·29	0·58	0·074	1·16	9·9
432	0·30-0·39	0·66	0·074	1·18	9·5
204	0·40-0·49	0·71	0·075	1·17	9·4
84	Over 0·49	0·78	0·075	1·15	9·2

cates a falling total iron in the primary slag with increasing silicon (and manganese) in the metal from the mixer. It does not, however, cover the wide ranges of total iron met with in Table VII. for several reasons, an obvious one being that efforts are made to melt the charge reasonably close to the final tapping composition, so that melts which would be very hard are fed with ore or scale, whilst prospective soft melts have further additions of iron before the primary slag is removed. An examination of individual results where slag samples are taken some time prior to slag-off does definitely indicate low slag irons with "strong" mixer metal and highly oxidised slags when the silicon is low. The damping effect of pre-slaggering adjustments then brings these effects down to the order of the figures shown in Table VIII.

The possibility of adjusting the slag iron to a constant figure before removing the slag has been definitely considered. It is difficult to accomplish economically, because as the slag iron is a function of the slag acids limestone may be required, or conversely may be in excess, and the adjustment of the oxide in the primary slag would be somewhat similar to the formation of a "primary refining" condition. If possible, it is better that constancy should come from constant quality of the ingoing iron.

In the foregoing outline, the application of slag control to the ordinary types of steel has been described. For this purpose, a figure for the total  $\text{SiO}_2 + \text{P}_2\text{O}_5$  of 23% is quite satisfactory for refining. Other figures are used for other qualities, high-carbon steels working down to figures between 18 and 20%; the principles of application are, however, the same. For high-carbon steels some

charging modification is also necessary to ensure a low-phosphorus melt; the conditions necessary to attain this can be deduced from the appropriate graphs shown above.

### *Conclusions.*

(1) These notes contain little that is new. In these days, however, when so much is known in theory and so little used in practice, this implies little disadvantage. The calculations are not mathematically correct, but they supply a means whereby the practical man can, with 95% certainty, make the correct addition to his furnace, without calling unduly on his memory or experience. It is another responsibility taken from him, thus allowing him to concentrate to a still greater extent on the factors in steel-furnace operation which cannot as yet be reduced to simple graphical methods of operation. The slow development over two years has been necessary to establish firmly the various phases for the operating personnel.

(2) The net refining time has been reduced from an average of 135 min. to 78 min., the latter being an average over 16 months, and equal to 75-100 tons per furnace week on refining alone. It is difficult to give figures for any possible savings due to the method of charging, on account of the numerous other factors also involved. There is no reason whatever to think that any output has been lost at this stage, however.

(3) A definite relationship appears to exist between the slag iron and the total  $P_2O_5 + SiO_2$  in the various slag groups. These acids can vary considerably with little alteration in the lime content of the slag.

(4) Fig. 12 shows a good relationship between the carbon and phosphorus in the bath and the iron in the primary slag when the furnace is clear melted, of a good heat and boiling freely.

(5) Fig. 13 reveals the tendency of the characteristics of the primary slag, as shown by the total iron, to persist through the refining and on to the tapping slags.

(6) Fig. 14 indicates the ratios between the tapping- and refining-slag irons and the phosphorus and manganese in the metal; also, the middle curve compares the phosphorus in the bath before slag-off with the iron taken at the same time. The difference between the two phosphorus curves for the same slag iron content is no doubt due to the slight difference in slag composition at the two periods. There are good reasons for believing that the temperature of the steel at the two stages will differ by no more than 20-25° C.

(7) All the analyses available are here published and may be of use in future statistical work on slags.

(8) The considerable steel production represented by these figures should be noted, as each cast represents an average of some 250 tons of ingots.

*Acknowledgments.*

The author is indebted to Mr. W. B. Baxter, Director and General Manager of the Appleby-Frodingham Steel Co., Ltd., for permission to publish this paper, to Mr. R. C. Badsey, one of the author's assistants, and to the sample passers and meltters, who carefully and conscientiously made the early trials in this departure from current practice.

APPENDIX I.—*Calculation of the Limestone for a Charge.*

<i>Charge.</i>	Tons.
Molten mixer metal, silicon 0·3%, phosphorus 1·25%	175
Scrap (mild steel) . . . . .	75
Total charge . . . . .	<u>250</u>
<i>Limestone Required.</i>	Boxes.
Mixer metal—for phosphorus only (Fig. 7)	19
Scrap (own mill scrap) . . . . .	Nil
Oxides : SiO <sub>2</sub> 3·0% ; P <sub>2</sub> O <sub>5</sub> 0·11% . . . . .	4·5
Silica, &c., from furnace . . . . .	0·9
Bricks from metal ladles, chutes, &c. . . . .	0·1
	<u>24·5</u>
Less allowance for dolomite (56 lb./ton steel) . . . . .	7·0
Total limestone required . . . . .	<u>17·5</u>

Thus, the above charge requires 17½ boxes of limestone. From this, however, is deducted the excess lime that had been added to the refining slag from the previous charge. Assume this were 2 boxes; the charged limestone would then be 15½ boxes.

*Limestone* for the *silicon* in the mixer iron is added after most of the charging is finished, and is adjusted according to the silicon in the iron charged—see Fig. 8.

Additions made in the above case would be a further 4 boxes of limestone with the last charging metal to compensate for the mixer silicon.

# PROGRESS IN THE CORROSION RESEARCH SECTION AT CAMBRIDGE UNIVERSITY.<sup>1</sup>

BY U. R. EVANS, Sc.D., M.A. (CAMBRIDGE UNIVERSITY).

*Paper No. 12/1943 of the Corrosion Committee.*

## SUMMARY.

The paper summarises results of investigations published since 1935 by twenty-four experimenters in sixty-four papers scattered through different journals. The research policy has been to study scientific causes and then to apply the results to practical problems; success or failure attending the applications provides a check on the accuracy of the scientific conclusions.

The electric currents flowing over the surface of metal corroding in salt solution have been measured, and found strong enough to account for all or nearly all the attack actually produced; corrosion is only seen at those points which the electrical apparatus indicates as anodic, and everything points to an electrochemical mechanism. Numerous measurements of "probability" and "conditional velocity" have been made, and the distinction between these two conceptions clears up many points which have hitherto appeared paradoxical; it shows why on iron partly immersed in a salt solution the water-line zone is immune in the early stages and strongly attacked later, and indicates that oxygen is at once a stimulator in increasing conditional velocity and an inhibitor in diminishing the probability. Sulphides in the metal or hydrogen sulphide in the liquid stimulate, under many circumstances, both the probability and the conditional velocity; the presence of copper in the steel or tin salts in the liquid largely counteracts the bad effect of sulphur, by fixing it in a stable form.

Electrochemical principles, borne out by practical experiments, indicate that anodic inhibitors may be "dangerous," since they localise and intensify attack if added in insufficient amounts. An experimental classification of inhibitors as "anodic" and "cathodic" has been carried out, and many attempts have been made to find an inhibitive system which would be both safe and efficient. The latest results are encouraging.

About 3000 painted steel specimens have been exposed out-of-doors at different stations, and certain combinations of coats have given good protection over seven years in London; the presence of partly removed mill scale is prejudicial to good results. New compositions, including zinc-rich organic paints, emulsion paints and inorganic (cementiferous) paints, are being developed for special purposes. Laboratory investigations regarding the causes of blistering and the anti-corrosive action of certain lead compounds are in progress.

Much work has been conducted on steel covered with metallic coats, including galvanised iron and tinplate; the behaviour of the latter in canning varies with the composition of the steel basis.

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<sup>1</sup> Received September 8, 1943. This paper is published by authority of the Corrosion Committee. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

In researches on corrosion-fatigue, new methods have been developed for feeding the corrosive liquid on to the specimen, giving a sharp water-line. The results show that corrosion-fatigue life can be greatly prolonged by contact with zinc or by paints pigmented with metallic zinc.

Electrochemical methods of estimating the thickness of thin films have been developed and compared with other methods. These have been used to study the thicknesses of interference-colour films, and also to follow the oxidation of iron exposed at ordinary temperatures (where the oxide remains invisible) as well as at higher temperatures. Methods have been worked out for transferring the films to celluloid. Several theoretical papers have been written on the laws governing film growth, and these largely academic lines of thought have led to a method known as "selective oxidation," which has greatly reduced the high-temperature oxidation of copper and the low-temperature tarnishing of silver. It has not yet been applied to ferrous materials.

#### FOREWORD.<sup>1</sup>

BY DR. W. H. HATFIELD, F.R.S. (CHAIRMAN OF THE CORROSION COMMITTEE).

THE work of Dr. U. R. Evans and his collaborators in the Corrosion Research Section of Cambridge University is too well known to need any introduction to those interested in metallic corrosion. The value of this work has long been recognised by all concerned with this field both at home and abroad, and new developments in the Cambridge studies have been followed with the keenest interest.

Dr. Evans possesses in high degree the imaginative insight which has enabled him to pick out and focus attention on the important factors underlying the often complex mechanism of corrosion, and to devise key experiments, often of striking simplicity, to illustrate and prove his arguments. To mention only one instance, the invaluable pioneer work in regard to the nature and significance of passive films at once comes to mind. But Dr. Evans' interests have been by no means confined to any single aspect of corrosion, and papers have been published on a wide variety of subjects, including the behaviour of protective paints and metallic coatings, the practical applications of soluble inhibitors and many aspects of corrosion testing and behaviour. It is, therefore, particularly interesting and valuable to have this review of the work during the period from 1935 to the present time. Such a consideration assists greatly in visualising the general relation between these various researches and the trend of the work as a whole. It is clear that the work has followed a definite connected plan and has registered important advances on a broad front.

Dr. Evans has been a member of the Joint Corrosion Committee of The Iron and Steel Institute and the British Iron and Steel Federation since its inception in 1928, and has always taken the

<sup>1</sup> Written shortly before Dr. Hatfield's death on October 17, 1943.

keenest interest in the work, contributing himself in no small degree, particularly in regard to the various laboratory studies both as an investigator and as Chairman of the Laboratory (Corrosion) Research Sub-Committee. The members of the Committee have fully recognised the very considerable importance of the fundamental studies and general laboratory work carried out in the Cambridge Corrosion Section, and have been very glad to be able to confirm their interest in the work by means of the financial support referred to by Dr. Evans in his Introduction. It is hoped that there will be a steady continuance of this close association and co-operation. Several of the present studies show definite indications of yielding results of much practical importance, and their further development will be awaited with the greatest interest.

#### AUTHOR'S INTRODUCTION.

At a meeting of the Corrosion Committee<sup>1</sup> held at Sheffield on July 26, 1943, it was proposed by Dr. G. D. Bengough, F.R.S., and unanimously resolved, that the author should be invited to prepare a summary of the corrosion researches carried out at Cambridge University during recent years. This invitation, which is greatly appreciated, has resulted in the present paper. It has been convenient to start the discussion at 1935, since a report on the general position was issued by the author<sup>2</sup> that year; moreover, the period 1935–1943 roughly corresponds with that during which generous financial support has been received from the Committee, since this support commenced in 1936.

The account which follows will, however, include also researches on the corrosion of non-ferrous metals sponsored by other bodies, such as work on preventing tarnishing of silver carried out by Dr. L. E. Price and Dr. G. J. Thomas for the Worshipful Company of Goldsmiths, several investigations by Dr. T. P. Hoar for the International Tin Research and Development Council, and by Mr. S. C. Britton for the British Non-Ferrous Metals Research Association. Most of the other work has had the support of the Iron and Steel Industrial Research Council, through The Iron and Steel Institute, Dr. A. J. Gould's work on corrosion-fatigue being sponsored by the Alloy Steel Research Committee of the Institute, and the other researches by the Corrosion Committee. Special acknowledgment should be made of the help and encouragement of Dr. W. H. Hatfield, F.R.S., Chairman of both Committees.

Since 1935, sixty-four papers or letters representing work or thought in the Cambridge Corrosion Section have appeared in recognised journals. Most of these have been joint papers by the

<sup>1</sup> A Joint Committee of The Iron and Steel Institute and the British Iron and Steel Federation, reporting to the Iron and Steel Industrial Research Council.

<sup>2</sup> U. R. Evans, *Science Progress*, 1935, vol. 29, p. 395.

author with one or more collaborators. Some stand in the author's name alone, and several in other names. In all cases, however, there has been friendly exchange of ideas between members of the Corrosion Section, so that almost every paper owes much to persons whose names do not appear below the title. Of the sixty-four papers, only nine have appeared since September, 1939; for obvious reasons, it has been permissible to publish very little of the work carried out since the outbreak of hostilities.

A discussion of work conducted within a limited period in a single laboratory would not be intelligible without some reference to work carried on outside the period and outside the laboratory in question. Inevitably, therefore, the present paper makes mention of earlier ones from Cambridge, and of papers from other laboratories published during the period under review (to avoid claiming credit for work done elsewhere the location has then been indicated). Apart from this, no attempt has been made to give any account of the vast amount of valuable work carried out in laboratories other than Cambridge, but the author would like to record his appreciation of the great kindness which he has received from those working on the subject in all parts of the world. He would also return thanks to Dr. G. D. Bengough and Dr. W. H. J. Vernon for several suggestions regarding the present report, to Dr. R. S. Thornhill for drawing Figs. 1 and 6, and to the Chemical Society for permission to reproduce Figs. 2, 3, 4 and 7. Finally, he would express his sincere gratitude, for help and encouragement throughout the period under review, to Dr. R. S. Hutton, Goldsmith Professor of Metallurgy, and Dr. H. McCombie, Reader in Chemistry at Cambridge University.

### I.—WET CORROSION.

(a) *Research before 1935.*—The earlier experimental work at Cambridge and elsewhere had indicated that the corrosion of metals by salt solutions was largely an electrochemical process, and a graphical construction introduced by the author<sup>1</sup> had proved convenient for expressing the manner in which polarisation and resistance may be expected to determine the corrosion rate (see Fig. 1). The corrosion velocity developed must correspond, in the sense of Faraday's law, to a current of that value  $i$  which will produce an intercept between the anodic and cathodic polarisation curves equal to  $iR$ , where  $R$  is the resistance of the circuit. The fact that the corrosion velocity does closely correspond to that calculated from electrochemical measurements had been established by the experiments of Hoar,<sup>2</sup> but the methods used had depended on the cutting of the specimen along the boundary separating anodic

<sup>1</sup> U. R. Evans, *Journal of the Franklin Institute*, 1929, vol. 208, p. 45.

<sup>2</sup> U. R. Evans and T. P. Hoar, *Proceedings of the Royal Society*, 1932, A., vol. 137, p. 343.

and cathodic areas; such a procedure is only applicable where these boundaries can be foreseen. It seemed important to measure corrosion currents without the cutting of specimens, and much of the work during 1935–1939 represented attempts to do this.

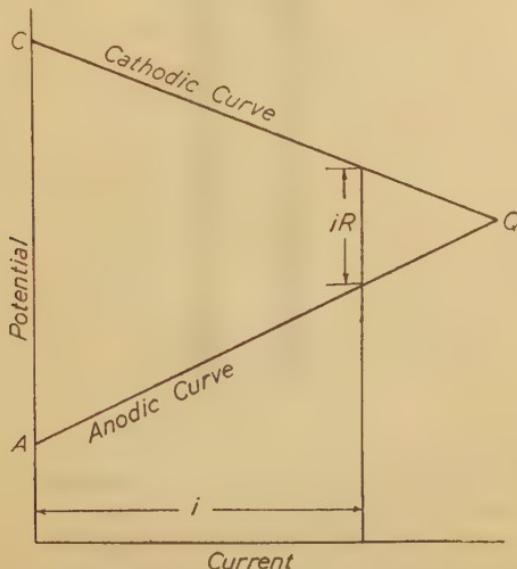


FIG. 1.—Geometrical Construction showing how Resistance and Polarisation Determine Corrosion Velocity.

(b) *Corrosion Currents around Scratch-Lines on Iron.*—The author<sup>1</sup> noticed in 1935 that if a fresh scratch-line is engraved on iron previously exposed to air, and if the specimen is covered with filter paper soaked in sodium bicarbonate solution just between “activating” and “passivating” concentrations, rusting takes place along the scratch-line, and generally nowhere else. If this rusting is of an electrochemical character, electric currents should presumably be passing through the filter paper from the scratch-line as anode to cathodic regions on either side. This was proved to be the case by means of the “dielectrode” shown in Fig. 2, which diverted a small fraction of the current through a microammeter, returning it to the filter paper about 2 mm. away; the use of two non-polarisable copper/cuprous-oxide electrodes served to avoid a counter-e.m.f. Since, however, only a fraction of the total current was diverted, the readings had no absolute meaning until the instrument had been calibrated upon similar wet filter paper along which known currents were passed from an external source. Experiments with continuous calibration were carried out by Thornhill<sup>2</sup> which placed the relation between current and

<sup>1</sup> U. R. Evans, *Nature*, 1935, vol. 136, p. 792.

<sup>2</sup> R. S. Thornhill and U. R. Evans, *Journal of the Chemical Society*, 1938, p. 614.

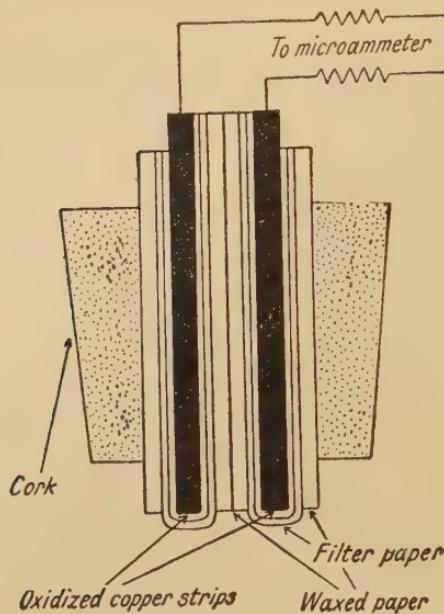


FIG. 2.—Dielectrode for Tapping a Fraction of the Current Flowing around a Scratch-Line on Iron (from *Journal of the Chemical Society*, 1938, p. 615, Fig. 1).

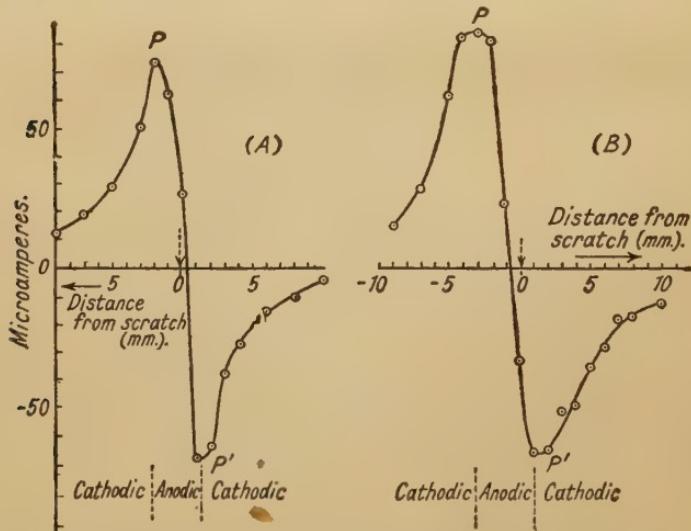


FIG. 3.—Currents Flowing around a Scratch-Line 2 cm. Long, (A) in early stages, (B) in later stages of corrosion (from *Journal of the Chemical Society*, 1938, p. 617, Fig. 3).

corrosion on a quantitative basis; he obtained curves such as Fig. 3, which show the current flowing outwards from the scratch-

line as anode. Application of Faraday's law indicates *the currents to be sufficiently powerful to account for the whole of the corrosion measured*, although the fact that iron has two electrochemical equivalents leaves an element of doubt. It was therefore decided to study zinc, which has only one electrochemical equivalent.

(c) *Electrochemical Study of the Corrosion of Zinc.*—A dielectrode constructed by Thornhill<sup>1</sup> for the exploration of zinc specimens standing vertically in dilute chloride solutions is shown in Fig. 4.

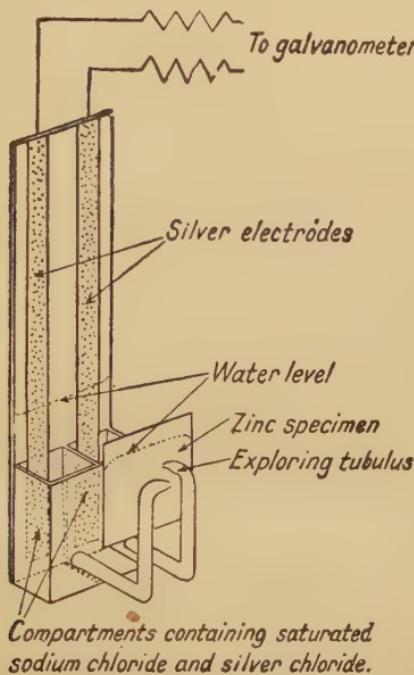


FIG. 4.—Dielectrode for distinguishing Anodic and Cathodic Points on a partly immersed vertical zinc surface (from *Journal of the Chemical Society*, 1938, p. 2111, Fig. 1).

It consists of two silver/silver-chloride electrodes, each furnished with a tubulus; the tip of one was pressed against the zinc at a chosen point, whilst the other remained slightly further away. Clearly, if no corrosion current existed, this symmetrical arrangement would give no deflection; if current was flowing to or from the point in question a deflection would be registered, the direction indicating whether the point was anodic or cathodic. In order to tap detectable currents it was necessary to fill the tubuli with liquid more concentrated than the corrosive solution, and this made the apparatus suitable only for qualitative purposes. Nevertheless, the demonstration of the electrochemical mechanism was impres-

<sup>1</sup> R. S. Thornhill and U. R. Evans, *Journal of the Chemical Society*, 1938, p. 2109.

sive; corrosion was observed only at those points which the electrical instrument showed to be anodic; at cathodic or neutral points no attack took place.

To obtain a quantitative relation between currents and corrosion, Agar,<sup>1</sup> using a single travelling electrode, traced out equipotential surfaces in the liquid, obtaining curves similar to that shown in Fig. 5. The direction of the current (at right angles to the equi-

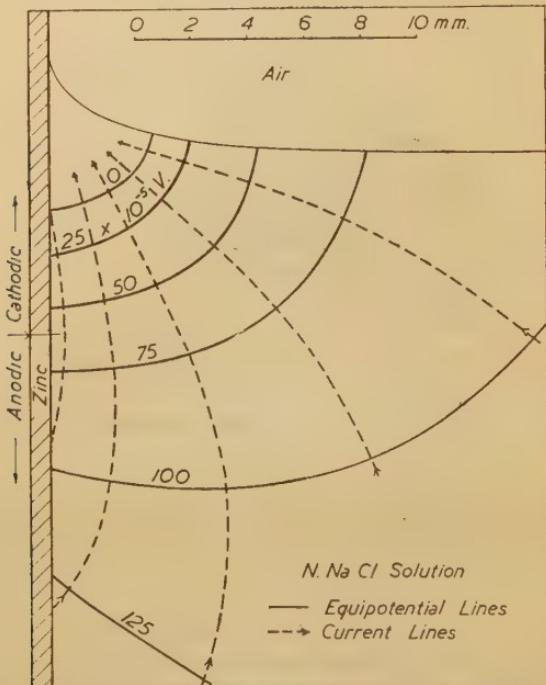


FIG. 5.—Potential Distribution and Current-Flow around Zinc Corroding in N Sodium Chloride Solution (from *Journal of The Iron and Steel Institute*, 1940, No. I., p. 223 P, Fig. 3).

potentials) is shown in broken lines. The distance between the various equipotentials gives a measure of the current flowing. The work was interrupted by the outbreak of war, but it had reached a stage at which there was no reasonable doubt that the currents accounted for the whole of the corrosion leading to a loose corrosion product; the small amount of highly adherent corrosion product formed above the water-line has probably a somewhat different mode of origin.

(d) *Measurements of Probability and Velocity.*—In assessing the expected damage to a metal placed in a given solution, it is neces-

<sup>1</sup> J. N. Agar, unpublished work summarised by U. R. Evans, *Journal of The Iron and Steel Institute*, 1940, No. I., p. 221 P.

sary to know (1) the *probability* that corrosion will start at all, and (2) the *conditional velocity* with which it will proceed, if it does start (this velocity is not necessarily constant in time). Often it is fairly certain that corrosion will start somewhere, and will then spread out. But if the exposed area is very small (*e.g.*, a gap in a paint coat), or if the liquid contains an inhibitor, it is by no means certain that attack will begin at all, and in such cases measurements of probability become important.

Mears<sup>1</sup> developed a method of measuring probability and conditional velocity concurrently on an iron plate. He ruled two sets of lines at right angles in wax, and then placed the specimen in a vessel which was filled with the desired gas mixture. The corrosive liquid was run in, and the excess run off by tilting the vessel; this left a "chess-board" of square drops on the specimen. The probability was obtained directly by counting the proportion of drops which produced corrosion, whilst the conditional velocity was obtained by estimating the metal in the corrosion product.

It was soon found that *probability and conditional velocity did not run parallel*. In oxygen-nitrogen mixtures, velocity increased and probability diminished as the oxygen concentration was raised. This seems to show that the longstanding debate as to whether oxygen, which undoubtedly often acts as a stimulator of corrosion, might sometimes be an inhibitor, is really a matter of definition. Oxygen is an accelerator in the sense that it generally increases velocity, but an inhibitor in the sense that it often diminishes probability. In a combination of metal and liquid where corrosion is certain to occur somewhere, the inhibitive character disappears altogether.

Mears studied the effects of numerous factors on the probability and corrosion velocity of steel. In each series of experiments all the factors except one were maintained constant, so as to isolate the effect of the variable. After studying the influence of constituents of the gas and liquid phases, he passed to the effect of minor constituents in the steel,<sup>2</sup> the results being analysed statistically by calculating the correlation coefficient. It was found that sulphides in the metal had a *marked effect in increasing probability*, and the same increase in probability was obtained even when particles of ferrous or manganese sulphide were suspended on a waxed-paper bridge passing through the drops but out of contact with the metal. Probably it is due to hydrogen sulphide formed by hydrolysis, since a mere trace of hydrogen sulphide introduced into drops of sodium bicarbonate greatly enhanced the probability, equivalent traces of sulphuric acid being without effect.

The influence of the various constituents of steel on corrosion

<sup>1</sup> R. B. Mears and U. R. Evans, *Transactions of the Faraday Society*, 1935, vol. 31, p. 527.

<sup>2</sup> R. B. Mears, *The Iron and Steel Institute, Carnegie Scholarship Memoirs*, 1935, vol. 24, p. 69.

by organic acids has been studied in great detail by Hoar and Havenhand.<sup>1</sup> The surface exposed to corrosion was fully immersed, and in these acid solutions corrosion was certain to occur, so that only velocity had to be measured. A calculation of correlation coefficients of different orders between the contents of various elements and the velocity measured indicated that here also the presence of much *sulphur* in the metal usually led to rapid corrosion. This was probably due to the formation of traces of hydrogen sulphide. When much *copper* was present, the bad influence of sulphur was found to be overcome, probably because the sulphur was then held as relatively stable copper sulphide. The fact that the presence of a *tin* salt in the solution undoubtedly diminishes

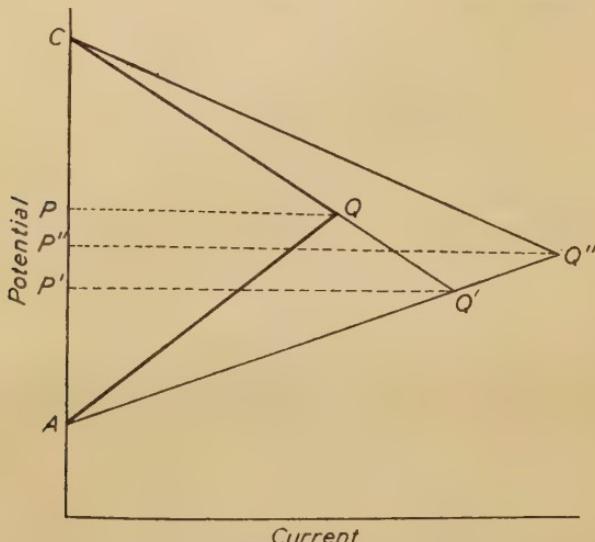


FIG. 6.—Geometrical Construction showing the Stimulation of Attack of Acids on Steel by (i) sulphides, (ii) massive cementite.

corrosion was ascribed by Hoar to precipitation as stable tin sulphide. In later work with Morris and Adams,<sup>2</sup> *phosphorus* was shown to be an important accelerator, and the conditions under which sulphur or phosphorus is the more important influence were clarified.

Hoar attributes the accelerating effect of hydrogen sulphide to decrease in the anodic polarisation. The conductivity of these liquids is so good that the corrosion velocity may be taken as the intersection of the anodic and cathodic polarisation curves (Fig. 6); the  $iR$  intercept is so small that it can be neglected. The addition

<sup>1</sup> T. P. Hoar and D. Havenhand, *Journal of The Iron and Steel Institute*, 1936, No. I., pp. 239 p., 283 p., especially p. 290 p.

<sup>2</sup> T. P. Hoar, T. N. Morris and W. B. Adam, *Journal of The Iron and Steel Institute*, 1939, No. II., p. 55 p.; 1941, No. II., p. 133 p.

of hydrogen sulphide to an acid liquid will flatten the anodic polarisation curve from  $AQ$  to  $AQ'$ , thus increasing the corrosion rate from  $PQ$  to  $P'Q'$ . Provided that all the steels have the same cathodic-polarisation curve, it follows that a simple measurement of electrode potential of the corroding specimen should serve directly to indicate the corrosion velocity. This would be most convenient, since electrode potentials can be measured very quickly. Investigations showed that for most steels the potential plotted against velocity did fall close to a single curve; steels containing massive cementite corrode somewhat more quickly than the potential would seem to indicate, probably because cementite reduces cathodic polarisation, shifting the curve from  $CQ$  to  $CQ''$ , and thus, for a given sulphur content, increasing the corrosion-velocity from  $P'Q'$  to  $P''Q''$ .

(e) *Distribution of Attack at Different Stages.*—The “expected” intensity of attack at any point must depend on both probability and velocity. The author<sup>1</sup> showed that in an experiment lasting time  $T$  it should be :

$$uT - \frac{u}{p}(1 - e^{-pT}),$$

where  $p$  measures probability and  $u$  velocity. The validity of this expression is independent of any particular theory of corrosion, and merely makes the assumptions about mutual independence of events which are customary in probability arguments, but which may not always be justified. If the expression is accepted, and combined with our knowledge of the electrochemical mechanism, the conclusion emerges that the water-line of steel or zinc partly immersed in a potassium or sodium salt solution will generally be unattacked in the early stages and severely attacked in the later stages of an experiment. This agrees with the experimentally established facts. Until recently the immunity of the water-line zone in the early stages, contrasted with the perforation sometimes developed in this part in the later stages, had seemed to suggest that the mechanism of corrosion must alter as time went on. It is now seen that a single theory is adequate to cover both stages. Similar arguments lead us to expect that when an inhibitor is present in amounts just insufficient to stop attack altogether, corrosion will be greatest at the water-line even from the outset; this also accords with experimental facts.<sup>2</sup>

The electrochemical experiments mentioned above showed that on partly immersed vertical plates the main cathodic area usually falls along the water-line, where oxygen, the cathodic stimulator,

<sup>1</sup> U. R. Evans, *Nature*, 1942, vol. 150, p. 151. *Journal of The Iron and Steel Institute*, 1942, No. II., p. 82 F.

<sup>2</sup> U. R. Evans, *Journal of the Society of Chemical Industry*, 1925, vol. 44, p. 165 T; 1927, vol. 46, p. 347 T. *Transactions of the Liverpool Engineering Society*, 1926, vol. 47, p. 218.

R. S. Thornhill, *Journal of The Iron and Steel Institute*, 1942, No. II., p. 94 F.

is most readily replenished (sometimes it may even rise above the original water-line, owing to creepage of alkali up the originally dry metal). In a sodium or potassium salt solution, the alkali here formed by the cathodic reaction protects the metal for considerable periods, precipitating any metallic salts in physical contact with the metal and thus stifling corrosion; in such solutions there is thus a considerable immune zone. If ammonium salts be introduced, even in small amounts, the corroded zone reaches the water-line<sup>1</sup> (the precipitating power of ammonia being less), whilst in calcium or magnesium salt solutions, including the water formerly supplied to the town of Cambridge (essentially calcium bicarbonate solution), the protected zone is a strip about 1 mm. broad along the meniscus.<sup>2</sup>

Currents set up by local differences in oxygen replenishment have long been known at Cambridge as "differential aeration currents." The oxygen concentration is only one of many factors which affect potential, and much discussion has taken place between the Teddington and Cambridge laboratories regarding the relative importance of various factors under different conditions. It is satisfactory to record that this led to agreement on the greater part of the subject—embodied in a joint paper by four authors, two from each laboratory.<sup>3</sup>

(f) *Necessity for Experiments in Multiple.*—Part of the uncertainties of the situation have been due to lack of experimental reproducibility met with in some, but not all, phenomena. The author<sup>4</sup> published some discussions of the cause of the variation, based on probability principles, and Mears and Daniels<sup>5</sup> calculated the "probable error" of all the Cambridge measurements up to 1935. The conclusion reached was that, in many cases, it is highly desirable to conduct experiments "in large multiple," and this may apply not only to measurements of velocity but also to experiments designed to study electric currents. In connection with discussions of differential aeration currents, Black<sup>6</sup> set up twenty-four cells each consisting of two co-planar vertical strips in sodium chloride solution, the upper one passing through the water-line; the two segments were connected to a milliammeter. These were studied for 28 days under thermostatic conditions. A few cells gave irregular results at first, but from the fourth to the twenty-eighth day all twenty-four cells were furnishing current in the same

<sup>1</sup> S. C. Britton and U. R. Evans, *Transactions of the Electrochemical Society*, 1932, vol. 61, p. 452.

<sup>2</sup> U. R. Evans, *Journal of the Society of Chemical Industry*, 1928, vol. 47, p. 57 T.

<sup>3</sup> G. D. Bengough, U. R. Evans, T. P. Hoar and F. Wormwell, *Chemistry and Industry*, 1938, Nov. 5, p. 1043.

<sup>4</sup> U. R. Evans, *Transactions of the Electrochemical Society*, 1930, vol. 57, p. 407; 1935, vol. 68, p. 384. *Engineer*, 1942, vol. 173, p. 143.

<sup>5</sup> R. B. Mears and H. E. Daniels, *Transactions of the Electrochemical Society*, 1935, vol. 68, p. 375.

<sup>6</sup> U. R. Evans and A. N. Black, *Engineering*, 1935, vol. 140, p. 86.

direction, the upper (better aerated) electrode being the cathode. However, except in the case of iron so uniform that the anode-cathode boundary is reproducible (such as the material specially prepared by Dr. W. H. Hatfield for Hoar's early work), experiments of this type do not allow the whole of the corrosion current to be tapped, since there may be local anodes on the cathodic electrode.

(g) *Effect of Resistance on Corrosion by Stray Currents.*—The graphical construction embodied in Fig. 1 indicates that if the resistance is low, so that the intercept is small, the current will be not far below the limiting value represented by the intersection point,  $Q$ ; under such circumstances, a large diminution of the resistance, say, to one-tenth of its previous value, will only slightly increase the current. This is equally true whether the e.m.f. arises from an internal or external source. In the corrosion of buried pipes or cable sheaths by stray currents from tramways it is important to know to what extent these may be diminished by increasing the circuit resistances (e.g., by better street paving or better drained soils). Lewis<sup>1</sup> accordingly traced several plates of curves showing the effect of resistance ( $R$ ) on the current ( $i$ ) flowing between rods buried in damp sand, for different values of applied e.m.f. and also different geometrical arrangements of the rods relative to the surface and to one another. At high values of  $R$  it was found that  $iR$  was constant, but this was far from true when  $R$  became low.

(h) *Dezincification of Brass.*—It was shown in 1924 by Bengough and May<sup>2</sup> (at South Kensington) that the commonest reason why certain brass condenser tubes escaped the form of attack often known as "dezincification" was the presence of arsenic. Some doubt still remained, however, of the manner in which arsenic acts. Experiments by Fink<sup>3</sup> suggest that it is mainly an anodic inhibitor. Fink attributes the dezincification of non-arsenical brass to selective corrosion of a few zinc-rich points, leaving spots of residual copper, which later act as cathodes for the deposition of copper ions; thus the main mass of copper is a redeposition product, in accordance with the views of Bengough and May. Arsenic, when present, forms a film which prevents susceptible points from undergoing selective attack; general corrosion on the main mass of metal can still take place.

## II.—METHODS OF PROTECTION.

### (1) *Soluble Inhibitors.*

(a) *General.*—The electrochemical mechanism shows why certain solutions attack iron more rapidly than others. When, as in attack by sodium chloride, the anodic product (ferrous chloride) and

<sup>1</sup> K. G. Lewis and U. R. Evans, *Korrosion und Metallschutz*, 1935, vol. 11, p. 121.

<sup>2</sup> G. D. Bengough and R. May, *Journal of the Institute of Metals*, 1924, vol. 32, p. 160.

<sup>3</sup> F. W. Fink, *Transactions of the Electrochemical Society*, 1939, vol. 75, p. 441.

cathodic product (sodium hydroxide) are both freely soluble, the attack will proceed apace, notwithstanding that the two products may subsequently interact to give, in the presence of oxygen, the mixture of hydrated oxides known as "rust." But if, as in the case of zinc sulphate, the cathodic product is sparingly soluble, or if, as in the case of sodium phosphate, the anodic product is sparingly soluble, we get much less attack. Such substances frequently diminish or prevent corrosion when added to any water which is not too rich in corrosive salts; the two classes can be referred to as *cathodic inhibitors* and *anodic inhibitors*, respectively.

(b) *Properties of Cathodic and Anodic Inhibitors.*—Of the two classes, cathodic inhibitors are the less efficient, since only when a relatively thick film of cathodic product has been formed over the cathodic area will the corrosion rate fall off. A familiar example of a cathodic inhibitor is the calcium bicarbonate present in many natural waters. It is well known that hard waters usually cause less corrosion than soft waters; the corrosion reaction deposits calcium carbonate at the cathodic portions as soon as the alkali there formed raises the pH value (this calcium carbonate is afterwards converted to a clinging and rather protective form of rust by interaction *in situ* with iron salts, formed anodically). Protection will only be obtained if the water contains no more carbonic acid than is needed to stabilise the calcium bicarbonate; if a natural water contains more carbonic acid than this value it will not immediately produce a protective film on iron, and is capable of causing corrosion. Such waters are said to be "aggressive." The amount of excess carbonic acid needed to stabilise calcium bicarbonate (over and above that needed to convert calcium carbonate to calcium bicarbonate) increases with the amount of calcium bicarbonate present, so that when a water from a chalk well (which is initially non-aggressive, being in equilibrium with calcium carbonate) is softened by the base-exchange process, the carbonic acid present, unless simultaneously removed during the softening, is more than enough to stabilise the calcium bicarbonate remaining after treatment; thus the non-aggressive water becomes aggressive. This effect of softening has been discussed by the author<sup>1</sup> in a paper on water treatment. From the corrosion standpoint, base-exchange softening is less acceptable than soda-lime softening, which usually leaves the water non-aggressive.

Anodic inhibitors are more efficient. Small amounts of sodium phosphate, sodium hydroxide or potassium chromate, added to waters of low salt-content, allow iron to be kept in them indefinitely without any rusting. But early work at Cambridge<sup>2</sup> showed that

<sup>1</sup> U. R. Evans, *Journées de la Lutte contre la Corrosion*, 1938 : *Chimie et Industrie*, 1939, vol. 41, Apr., No. 4 bis, p. 492 c. *Chemistry and Industry*, 1941, vol. 19, p. 867.

<sup>2</sup> U. R. Evans, *Journal of the Society of Chemical Industry*, 1925, vol. 44, p. 167 T; 1927, vol. 46, p. 348 T.

if added in insufficient quantity they actually intensify attack, so that iron sheet is perforated more quickly than if no addition is made. The inhibitor diminishes the total attack, but diminishes still more the area upon which the attack is directed, so that the attack per unit area is enhanced. In a theoretical paper, the author<sup>1</sup> has shown that this intensification of attack by insufficient addition of inhibitor was to be expected—on electrochemical principles—for processes controlled by the cathodic reaction whenever the inhibitor employed was an anodic inhibitor; with a cathodic inhibitor no such intensification of attack is predicted by theory. Thus, *anodic inhibitors are efficient but dangerous*, whilst *cathodic inhibitors are inefficient but usually safe*; this deduction from theory agrees generally with practical experience of inhibitors in service. It should, however, be added that, if corrosion by a limited volume of water is allowed to run on until some corrosive substance (e.g., oxygen or carbonic acid) is completely exhausted, *any* substance which reduces the area undergoing attack *must* intensify the corrosion, whatever the mechanism.

(c) *Classification of Inhibitors.*—It has clearly become important to decide which inhibitors are cathodic and which anodic. For this purpose a special cell was developed, and Chyżewski<sup>2</sup> used it to classify a number of inhibitors. He found that sodium hydroxide and carbonate act as both anodic and cathodic inhibitors, zinc sulphate as a cathodic inhibitor only, and emulsifying oil as an anodic inhibitor. In the presence of alkali, a chromate inhibits the cathodic reaction, but in the presence of acid there is marked stimulation at the cathode; chromates act as anodic inhibitors in neutral, but not in acid, solutions.

(d) *Attempts to Obtain a Safe and Efficient System.*—One of the most pressing needs of the day is an inhibitive system *at once safe and efficient*, especially for use in cooling waters at industrial plants. A few years ago it seemed possible that this might be obtained by a combination of anodic and cathodic inhibitors. Hopes were entertained that a mixture of chromic acid with excess of magnesia ("basic magnesium chromate") might serve, and Thornhill<sup>3</sup> carried out a long series of experiments to discover whether additions of these chemicals, insufficient to stop corrosion altogether, increased or decreased the rate of thinning of iron sheet. A micrometer screw, provided with an electrical contact to give warning when it touched the bottom of a pit, was designed to measure loss of thickness. Unfortunately it was found that basic magnesium chromate, although decreasing the total corrosion, increased the depth of

<sup>1</sup> U. R. Evans, *Transactions of the Electrochemical Society*, 1936, vol. 69, p. 213.

<sup>2</sup> E. Chyżewski and U. R. Evans, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 215.

<sup>3</sup> R. S. Thornhill, *Journal of The Iron and Steel Institute*, 1942, No. II., p. 83 p.

penetration into the metal; thus it is, under stagnant conditions at room temperature, a dangerous inhibitor.

The localised attack met with in the presence of inhibitors often takes place at the water-line, and Thornhill studied the causes leading to water-line corrosion. Apart from those previously known, he noticed that if water condenses above the water-line it may trickle down and dilute the liquid in the meniscus zone, leading to the cell :

Iron | Concentrated inhibitor | Diluted inhibitor | Iron,

which, having a large cathode and small anode, will produce intense attack. This cause of corrosion will only exist in confined spaces where the metal has become colder than the liquid, but such a state of affairs is likely to arise in cooling systems containing an air space shortly after the operation of a plant has been suspended.

Some experiments carried out by Thornhill, assisted by A. Shadbolt, in which heat was conveyed to the liquid through the metal, thus reproducing conditions present in a cooling system, indicated that here basic magnesium chromate was relatively safe, and was surprisingly effective in putting a stop to rusting which had already commenced. It was expected that the use of inhibitors would have a marked effect—beneficial or otherwise—on heat transfer, but a number of measurements by Thornhill indicated that the effect was relatively small under the conditions studied.

Although the *simultaneous* addition of anodic and cathodic inhibitors had proved disappointing, it was decided to study the effect of *alternate* treatment with inhibitors of the two classes. Thornhill is now engaged on this investigation, which at the moment is yielding hopeful results. But it is too early to assert that an inhibitive system both safe and efficient has been arrived at.

(e) *Inhibitive Pretreatment*.—The researches just described are concerned with the effect of adding soluble inhibitors to a water which is causing trouble through corrosion. It would be satisfactory to find a chemical treatment which would leave iron or steel passive to natural waters containing no inhibitor. The author<sup>1</sup> has treated abraded steel with mixtures containing chromates and chlorides adjusted to dissolve away the most susceptible parts of the surface and leave the rest passive. After such treatment it was found that the period which elapses before the appearance of rust in most natural waters is increased about a hundredfold; but rusting is not prevented indefinitely.

Thornhill<sup>2</sup> has studied the protection of steel by coatings obtained through dipping in various solutions. After a detailed study of different liquids, a bath containing lead nitrate, zinc nitrate, ammonium nitrate and ammonium chloride was found to

<sup>1</sup> U. R. Evans, *Nature*, 1938, vol. 142, p. 160.

<sup>2</sup> R. S. Thornhill and U. R. Evans, Fifth Report of the Corrosion Committee, *The Iron and Steel Institute*, 1938, *Special Report No. 21*, p. 381.

be the best. Bolts and nuts immersed in this bath and then sprayed with a lanoline solution in toluene could be kept out-of-doors for over a year without seizing, much longer than if the lanoline solution alone was employed. Similar baths had some value as a pretreatment process for steel which was subsequently to be painted.

Other methods of preparing rusty steel for subsequent painting were developed by Thornhill.<sup>1</sup> He subjected the surface simultaneously to sprays of two different solutions (e.g., zinc sulphate and potassium chromate) chosen to precipitate an inhibitive substance (e.g., zinc chromate) within the rust. Another good combination was lead nitrate and sodium phosphate. It was found that single paint coats of iron oxide applied to a steel surface thus treated were much less damaged by under-rusting after 2½ years' exposure out-of-doors than similar paint applied to steel without pretreatment.

An important question affecting the practical use of chemical pretreatment is whether, if the treatment is applied wrongly (e.g., for too short a time), the attack may be confined to certain parts and therefore intensified, so that perforation occurs more quickly than if no pretreatment had been applied. Lewis<sup>2</sup> studied the effect of various chemical pretreatment processes on unalloyed magnesium, including some well-tried processes worked out in Dr. H. Sutton's laboratory at Farnborough, as well as a new pretreatment process developed at Cambridge, based on a bath containing zinc sulphate and ammonium nitrate. (This bath would probably need modification before it was suitable for magnesium alloys.) After treatment in the various baths for different periods, corrosion-time curves were obtained in sodium chloride solutions of different concentrations, and the period needed to produce perforation was determined. It was found that, although short periods of dipping generally produced less benefit than long periods, even the shortest periods of dipping were beneficial in lengthening the time needed for perforation. This was true of all the baths studied.

## (2) Paints.

(a) *Results of Seven-Year Exposure Tests.*—In the paint tests organised from Cambridge, about 3,000 specimens have been exposed at stations representing urban, marine, country and mixed climates; the chief station has been on the laboratory roof at Cambridge. The most important series wound up during the period under survey has been Britton's<sup>3</sup> seven-year tests on steel

<sup>1</sup> R. S. Thornhill and U. R. Evans, *Journal of the Society of Chemical Industry*, 1939, vol. 58, p. 13.

<sup>2</sup> K. G. Lewis and U. R. Evans, *Journal of the Institute of Metals*, 1935, vol. 57, p. 231.

<sup>3</sup> S. C. Britton and U. R. Evans, *Journal of the Society of Chemical Industry*, 1939, vol. 58, p. 92.

specimens covered with two or three coats of oil paints; examination of the specimens led to the following main conclusions:

(1) Improved protection was obtained by adding litharge to the red lead used as a primer below red iron oxide, despite the practical difficulty in using oil paints rich in litharge due to their rapid setting.

(2) Among priming coats tested below iron oxide covering coats, those pigmented with alloyed metallic lead behaved as well as red lead, although giving poor protection when used as a single coat. A mixture of zinc chromate and iron oxide gave better results than red lead as a priming coat in London, and as good results at Cambridge.

(3) The replacement, in both coats, of refined linseed oil by a mixture of tung oil and boiled linseed oil, in amounts chosen to compensate the expansion of the tung oil by the contraction of the linseed, conferred a marked increase in protective qualities.

(4) With nearly all paint combinations, the specimens on which the paint was applied over mill scale behaved worse than those descaled by grinding before painting. In no instance did the scale-covered specimen show a superiority over the corresponding descaled one, although the mill scale was almost unbroken at the time of painting. Nearly all the three-coat combinations applied to descaled steels gave almost perfect protection for seven years in London and Cambridge. Red lead covered with two coats of micaceous iron ore or red iron oxide can be recommended.

(5) Specimens carrying two coats naturally behaved less well than those with three, but one two-coat combination (red lead covered with micaceous iron ore) gave almost perfect protection to a descaled surface in London over seven years.

(6) The reproducibility between duplicates was good, and where the points tested overlapped with those under investigation in The Iron and Steel Institute Corrosion Committee's own tests, there has usually been good agreement. This appears to justify the adoption of the small size of specimen used in the tests organised from Cambridge.

(b) *Orders of Merit in Painted and Unpainted States.*—It has often been assumed that exposure tests upon metals in the unpainted condition will represent their relative merits in service, when they will be covered with paint. In 1935, no experimental justification existed for this assumption, and Lewis<sup>1</sup> therefore carried out some tests on a series of materials. It was found that after 2½ years' outdoor exposure the orders of merit in the painted and unpainted conditions were appreciably different, and that the

<sup>1</sup> K. G. Lewis and U. R. Evans, Third Report of the Corrosion Committee, *The Iron and Steel Institute*, 1935, *Special Report No. 8*, p. 177.

presence of scale had also an influence on the order; still greater differences were noted between the orders of merit obtained at different exposure stations.

(c) *Effect of Mill Scale below Paint.*—In another research, Lewis<sup>1</sup> studied the effect of mill scale on the rising of paint. Specimens from which the scale had been *partly removed* by weathering before painting behaved much worse than those which, at the time of painting, were either wholly covered with scale or had been completely descaled, by weathering, pickling or grinding. Paint applied to part of a surface carrying the scale intact showed undermining at the edge of the painted area, and some rising at points within it. It seems that it is not so much the scale but the holes in the scale which cause the intense local rusting with rising and failure of the paint; a small hole in a sheet of scale will produce the combination of small anode and large cathode which usually leads to intense attack.

These tests of Lewis seemed to suggest that descaling by long-period weathering could produce a satisfactory painting surface, but subsequent tests by Thornhill<sup>2</sup> showed that descaling by weathering was a somewhat haphazard method, since two series of specimens started on different dates behaved quite differently. In both cases the surface became completely covered with rust when only a small fraction of the area had been descaled, the rust coat hiding the scale and slowing down its further removal. Descaling by weathering seems to depend on the weather conditions at the time of first exposure. Hudson,<sup>3</sup> Official Investigator to the Corrosion Committee, is probably right in stating that, in general, weathering is an inferior method of descaling.

(d) *Causes of Inhibitive Action of Certain Lead Compounds.*—The outstanding performance of paints containing certain lead and other pigments, even when the paint films were clearly porous, made it advisable to study in the laboratory the mechanism of protection by these bodies. In 1934, Lewis<sup>4</sup> had carried out work in which steel specimens were shaken with air, water (or salt solution) and pigment in tubes, without any oil, so as to allow free access of corrosive influences to the metal; other experiments had consisted in placing drops of dilute salt solutions on painted steel plates, with a scratch-line traced through the paint so as to expose the steel. These experiments had made it clear that many pigments possessed a specific inhibitive effect, quite apart from the

<sup>1</sup> K. G. Lewis and U. R. Evans, Third Report of the Corrosion Committee, *The Iron and Steel Institute*, 1935, *Special Report No. 8*, p. 175.

<sup>2</sup> R. S. Thornhill and U. R. Evans, Fourth Report of the Corrosion Committee, *The Iron and Steel Institute*, 1936, *Special Report No. 13*, p. 175.

<sup>3</sup> J. C. Hudson, "The Corrosion of Iron and Steel," pp. 102, 116, 266. London, 1940 : Chapman and Hall, Ltd.

<sup>4</sup> K. G. Lewis and U. R. Evans, *Journal of the Society of Chemical Industry*, 1934, vol. 53, p. 25 T.

power of the paint films to exclude corrosive influences. Only certain lead compounds were inhibitors, some being even stimulators of attack. Mayne<sup>1</sup> is now carrying further the work on lead pigments. He finds that those pigments which possess inhibitive properties produce a colloidal substance, probably lead hydroxide, in water, and deposit a white solid, quite different from the original pigment; inhibitive properties only develop as these compounds appear, and they are probably to be regarded as the true inhibitors. Contact between the iron and the lead compound (or metallic lead powder, which possesses considerable inhibitive action) is not needed for inhibition, but the presence of salts is prejudicial to it.

(e) *Zinc-Rich Paints.*—Much work has been carried out on paints pigmented with zinc dust. With certain vehicles it has been found possible to introduce so much zinc dust that the particles are in metallic contact with one another, as shown in electrical tests by Mayne.<sup>1</sup> Such coats, if applied directly to clean steel, will confer protection even at gaps in the coat. Zinc-rich paints, however, protect against sea water even when applied to rusty steel. Mayne showed that, although in such cases there is no electrical contact between zinc and iron at the outset, this contact develops later, apparently through the reduction of the rust to magnetite or perhaps metallic iron, which serves to connect the zinc to the steel basis. Still later, the electrical contact disappears again, but protection continues, probably because zinc hydroxide has been deposited upon the steel as cathode.

(f) *Causes of Blistering.*—The experiments just described refer not only to commercial zinc-pigmented paints but also to new paints compounded at Cambridge. There is one great disadvantage to all this class of paint, namely, the formation of blisters. This is also being examined by Mayne, who finds that blisters can be produced in certain clear varnish films, even when zinc is absent. The blisters contain alkaline liquid, and probably represent specifically cathodic spots. The cathodic product (sodium hydroxide) will loosen the paint, and then, since, for reasons of electrical transport, the concentration next to the metal is greater than that outside, water will be drawn in by osmosis. A similar concentration difference will be set up at anodic points, but the anodic product (ferrous chloride) will not loosen the paint, and the concentration difference will dissipate itself by the passage of salt outwards, giving rise to small rust nodules. Thus, there are two types of defect, differing in appearance, and associated with anodic and cathodic points, respectively. It seems possible that in the zinc-rich paints the alkali later attacks the zinc, producing hydrogen; but this, if it occurs, is a secondary effect.

Attempts are being made to correct the trouble. It will be noticed that the blisters are explained in the same way as the

<sup>1</sup> J. E. O. Mayne, unpublished work.

softening of paint around the edge of salt drops, studied in 1929 by the author.<sup>1</sup> This was undoubtedly due to the cathodic formation of alkali. Certain types of blistering noted near the water-line on partly immersed painted specimens were ascribed<sup>2</sup> in 1927 to the same cause.

(g) *Emulsion Paints.*—Early tests<sup>3</sup> had suggested that invisible films of moisture, present on specimens painted at dawn, were perceptibly harmful, as shown by comparison with specimens similarly painted in the afternoon. Mayne<sup>4</sup> has, therefore, produced a series of water-emulsion paints suitable for application to wet metalwork; under such conditions, the water on the metal should become merged with that already in the paint. Exposure tests, however, have not indicated that such paints are superior to conventional oil paints. There is little doubt that by hard brushing of a wet surface, water can be displaced by the oil paint, but the use of an emulsion paint under such conditions might save labour.

(h) *Cementiferous Paints.*—Another series of paints developed at Cambridge and suitable for application to wet, rusty and, in some cases, greasy surfaces is the so-called cementiferous paints. These are, in most cases, wholly inorganic, and are so compounded that, although no actual cement is included in the paint, oxy-chlorides, having cement-like properties, are obtained by reactions after the paint has been spread out on the metal. The aim has been to obtain this by an electrochemical mechanism, so that the cement will begin to be formed at the surface of contact, thus improving the adhesion. Oxychlorides are not in themselves inhibitors of corrosion—frequently they stimulate it—but, by arranging that there shall be excess of zinc dust in the paint after setting, good protection can be obtained, even if the coat after setting is definitely porous. If the paints are to be applied to a rusty surface, they should contain a compound of arsenic or antimony which facilitates the building of metallic bridges through the rust joining the zinc to the steel, as shown by electrochemical tests; if more convenient, one of these compounds can be applied as a wash previous to the application of the paint. One of these inorganic paints is already in use in a case in industry where local corrosion had been causing great trouble; latest reports are encouraging. These paints are, however, still in course of development, and a detailed description would be out of place.

<sup>1</sup> U. R. Evans, *Transactions of the Electrochemical Society*, 1929, vol. 55, p. 243.

<sup>2</sup> U. R. Evans and R. T. M. Haines, *Journal of the Society of Chemical Industry*, 1927, vol. 46, p. 365 T.

<sup>3</sup> U. R. Evans and S. C. Britton, *Journal of the Society of Chemical Industry*, 1930, vol. 49, p. 178 T; 1932, vol. 51, p. 212 T.

<sup>4</sup> J. E. O. Mayne, unpublished work.

(3) *Metallic Coats.*

(a) *Tinplate*.—In connection with the nationally important problem of canned food, Hoar<sup>1</sup> has carried out extensive tests on the behaviour of tinplate towards fruit juices. Laboratory tests conducted in the Corrosion Section and other laboratory tests by Morris at the Low Temperature Research Station (Cambridge) have been correlated with long-period storage of cans carried on by Adam at the Fruit and Vegetable Preservation Research Station, Chipping Campden, until failure, usually by hydrogen-swelling, occurred. Many different fruits have been used. The behaviour of the cans depends largely on the composition of the steel, and particularly on the content of copper and phosphorus (see Section I. (d)); the practical recommendations resulting from the tests are that the use of steel with high copper content (0·16–0·22%) and low phosphorus content (0·03–0·045%) should roughly double the expected life of the cans.

An interesting outcome of the research is that a short test consisting of two minutes' immersion in boiling dilute hydrochloric acid gives a far better indication of the merits of a steel as a material for canning fruit than does long-period testing in actual fruit juices (unless under anaerobic conditions); tests in the fruit acids are intermediate in value. The reason is simple. The cause of failure of the cans is connected with corrosion of the hydrogen-evolution type, and this type of corrosion is obtained by the short immersion in hot hydrochloric acid, and not in the longer test in fruit juice containing air.

(b) *Galvanised Iron*.—Research has been carried out by Britton<sup>2</sup> on the behaviour of galvanised iron in natural waters or solutions containing the salts present in natural waters. The protection is at first mechanical, but when at any point the steel, or the iron-zinc alloy layer, becomes exposed, the zinc will continue to confer "cathodic protection." Since, however, zinc is sacrificed in protecting the bare area, it is clear that this bare area must extend. Protection will cease as soon as the bare area becomes so large that the current density at its centre is insufficient to protect. If the zinc is thick, however, a protective coat of calcium carbonate or perhaps zinc hydroxide may already have been deposited by the cathodic reaction, which will not only postpone the attack upon the iron (or iron-zinc alloy) but will also slow down the anodic corrosion of the zinc coating. Whether this result can be achieved must depend not merely on the thickness of the zinc but on the hardness of the water; in general, a thicker coat is needed for protection against soft water than hard.

<sup>1</sup> T. P. Hoar, T. N. Morris and W. B. Adam, *Journal of The Iron and Steel Institute*, 1939, No. II., p. 55 P; 1941, No. II., p. 133 P.

<sup>2</sup> S. C. Britton, *Journal of the Society of Chemical Industry*, 1936, vol. 55, p. 19 T.

Britton<sup>1</sup> also developed an electrochemical test for measuring the thickness of a zinc coat based on the number of coulombs needed to destroy it.

#### (4) *Cathodic Protection.*

(a) *Protective Current Density.*—The protection of partly exposed steel through contact with zinc, mentioned above in connection with zinc-pigmented paint and galvanised coats, and discussed below in connection with corrosion-fatigue, is a special case of cathodic protection. In some cases it may be advantageous to use an external source of e.m.f.—as is now customary in America for the protection of water-tanks and pipelines. Many measurements of the current density needed for cathodic protection were made in early work at Cambridge both in acid<sup>2</sup> and in neutral<sup>3</sup> solutions. It was discovered that in salt solutions a much higher current density was needed under moving than under stagnant conditions, evidently owing to the dissipation of cathodically produced alkali, which would otherwise contribute appreciably to protection.

(b) *Theory of Cathodic Protection.*—The principles of cathodic protection have entered into Hoar's work on tinplate, since tin is anodic to iron in many fruit juices, and will, for a time, confer protection at pores in the coat. The theory of cathodic protection has been largely developed by Hoar,<sup>4</sup> who has elaborated the graphical method shown in Fig. 1 to interpret the more complicated case where two metals are in contact, each carrying a cathodic and anodic area. Further theoretical and practical work on the subject has been carried out, after his return to America, by Mears, in collaboration with R. H. Brown<sup>5</sup>; they show that, in order to obtain complete protection, the potential of the cathodic areas must be polarised to a potential equal to or more anodic than the open-circuit potential of the anodes.

### III.—CORROSION-FATIGUE.

(a) *Practical Importance of Corrosion-Fatigue.*—It is generally agreed that many service failures commence as corrosion-fatigue cracks, although doubtless the final breakage is often a simple shock or tensile fracture. The proportion of failures originating in conjoint (chemical-mechanical) action is likely to increase as the application of improved mathematical procedure to engineering problems teaches how to avoid purely mechanical failures. Never-

<sup>1</sup> S. C. Britton, *Journal of the Institute of Metals*, 1936, vol. 58, p. 211.

<sup>2</sup> U. R. Evans and J. Stockdale, *Metals and Alloys*, 1930, vol. 1, p. 377.

<sup>3</sup> U. R. Evans, *Metals and Alloys*, 1931, vol. 2, p. 62.

<sup>4</sup> T. P. Hoar, *Transactions of the Faraday Society*, 1934, vol. 30, p. 481.  
*Journal of the Electrodepositors' Society*, 1938, vol. 14, p. 33.

<sup>5</sup> R. B. Mears and R. H. Brown, *Transactions of the Electrochemical Society*, 1938, vol. 74, p. 519; 1942, vol. 81, p. 455.

theless, although much work had been devoted to the behaviour of different materials under corrosion-fatigue conditions and to the effect of different protective treatments, comparatively little fundamental was known in 1935 about the causes. Hence the Cambridge researches were undertaken.

(b) *Improved Methods of Feeding.*—In early work at Cambridge the fracture was frequently observed to occur at the margin of the wetted region. This suggested the desirability of a form of feeding arrangement which gave a well-defined, reproducible "water-line." Many of the feeding methods adopted in other laboratories—although well adapted for the several purposes of the investigators—were a little unsatisfactory in this particular respect. Gould therefore designed a feeding mechanism in which the liquid was applied by means of a cotton-tape sling passing below the wire specimen without actually touching it. Later Huddle<sup>1</sup> has developed a wick-feed for rod specimens which only approaches the rod at a single point, whilst in Tchorabdji's<sup>2</sup> work on wires the solution flows down a vertical glass rod, waxed all over except along the side nearest to the wire specimen, where an unwaxed channel provides a "roadway" for the liquid. In all three cases, the liquid is held by capillarity between the specimen on one side and the sling, wick or rod on the other, so as to cover, at the outset, a small, sharply defined area.

(c) *Study of the Mechanism.*—After a preliminary study of the effect of temperature on corrosion-fatigue,<sup>3</sup> Gould commenced a comprehensive research, carried out under thermostatic conditions, on the influence of various factors on corrosion-fatigue; an interim report<sup>4</sup> was published in 1939, but the work was soon afterwards interrupted by the war. The main researches were conducted on steel-wire specimens wetted with chloride-chromate solutions, and curves were published showing, at different stress ranges, the effect of varying chloride concentration at constant chromate concentration (including zero), and of varying chromate concentration at constant chloride concentration. In general, an increase of stress range and of chloride concentration shortens life, whilst an increase of chromate concentration lengthens it. The electrode potential of the wire was measured during the experiments with chloride-chromate mixtures; it first rose with time—pointing to a reinforcement of the film—and then somewhat suddenly collapsed, indicating a breakdown.

During the first stage (film reinforcement), the chromate is able to repair any incipient cracking which the alternating stress may cause, the film being thickened—doubtless by precipitation of a

<sup>1</sup> A. U. Huddle and U. R. Evans, *Journal of The Iron and Steel Institute*, 1944, No. I., p. 109 P (this volume).

<sup>2</sup> M. Tchorabdji, unpublished work.

<sup>3</sup> A. J. Gould, *Engineering*, 1936, vol. 141, p. 495.

<sup>4</sup> A. J. Gould and U. R. Evans, Second Report of the Alloy Steels Research Committee, *The Iron and Steel Institute*, 1939, *Special Report* No. 24, p. 325.

mixture of ferric and chromic oxides at the point of damage, as indicated by the earlier work of Hoar.<sup>1</sup> Now, a thick film is more liable to breakdown than a thin one—partly because it becomes less easy for the inhibitive substance to reach the metal at the bottom of incipient cracks threading a thick film, and partly because a thick film is less “braced” by the proximity of the metal. When the repair and thickening have proceeded too far, the film definitely breaks down, as shown by the “tumble” of potential, and the corrosion-fatigue cracking is able to start.

Preliminary experiments by Tchhorabdji in chloride solutions (free from chromate) appear to show that the actual rate of passage of iron into the combined state is not very much altered when the stress is increased. The effect of stress is apparently rather to change the *distribution* of corrosion, causing the attack to be directed on the point of high stress concentration, conferring thereby cathodic protection on the remainder of the surface, so that the total attack is not greatly increased by the stress. Thus—as has been well brought out by photographs made by McAdam and Geil<sup>2</sup> at Washington—instead of the hemispherical pits characteristic of stressless corrosion, alternating stresses produce fissures with pointed ends, which extend rapidly into the metal, leading to early failure.

(d) *Effect of Corrosion-Fatigue on Tensile Properties.*—It is a matter of practical importance to know whether the ordinary tensile properties of a steel bar subjected to alternating stresses under corrosive conditions suffer rapid deterioration. Tests by Huddle<sup>3</sup> on steel bars wetted with sea water indicate that up to about half the corrosion-fatigue life the tensile properties are almost unimpaired; thereafter the tensile strength falls perceptibly and the elongation at fracture seriously.

(e) *Prevention of Corrosion-Fatigue.*—Gould’s work confirmed the results of earlier investigators in showing that contact with zinc—even when it did not cover up the surface of the steel—prolongs the resistance to corrosion-fatigue in chloride solutions. There appeared, however, to be one possible danger in recommending zinc protectors for general use, since it was feared that contact of zinc with steel wetted by acid rain water would charge the steel with hydrogen which might embrittle the steel. This possibility was tested by Stuart<sup>4</sup> on a special corrosion-fatigue machine in which twenty thin steel strips could be subjected simultaneously to alternating bending in a thermostat room; care was taken that the stresses did not exceed the yield point. The steel strips were

<sup>1</sup> T. P. Hoar and U. R. Evans, *Journal of the Chemical Society*, 1932, p. 2476.

<sup>2</sup> D. J. McAdam and G. W. Geil, *Bureau of Standards Journal of Research*, 1940, vol. 24, p. 685.

<sup>3</sup> A. U. Huddle and U. R. Evans, *Journal of The Iron and Steel Institute*, 1944, No. I., p. 109 p (this volume).

<sup>4</sup> N. Stuart and U. R. Evans, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 131 p.

wetted with sulphuric acid of different concentrations (including a range higher than would ever occur in rain). Comparative experiments showed that contact with zinc prolonged the life at many concentrations, and at no concentration was the life seriously shortened. The effect of nickel contacts was also tested. Owing to the large scatter of results usually met with in corrosion-fatigue work, the "t-test" was used to distinguish "significant" from "non-significant" results.<sup>1</sup> The research showed that the danger of embrittlement by zinc contacts was not serious for bending in the elastic range; indeed, even steel highly supercharged with hydrogen by cathodic treatment in sulphuric acid containing arsenic had a long fatigue life when bent to and fro within the elastic limit, although it broke rapidly if bent beyond the yield point.

This danger having been disposed of, Huddle undertook measurements of the increase of life obtainable by applying a zinc-rich paint (either organic or cementiferous) to steel subjected to corrosion-fatigue in sea water. In one set of experiments the paint was applied to that portion of the steel which was to be wetted by the sea water, so that the paint conferred "mechanical exclusion" as well as "cathodic protection"; considerable increase of life was obtained, zinc-pigmented chloro-rubber and polystyrene paints being outstanding. But prolongation of life—which the t-test showed to be significant—was also obtained where the unpainted steel was fully exposed to the sea water, being merely joined electrically to an external strip of steel covered with zinc-rich paint (or in some experiments to a zinc strip); one zinc-rich cementiferous paint applied on the steel sheet gave almost as much increase of life as did the strip of zinc.

Tchorabdjii is measuring the effect of a cathodic current on the chemical attack on steel under alternating stress, and finds that to obtain a given diminution of corrosion rate, a much higher current is needed at high than at low stress ranges.

(f) *Other Types of Conjoint Action.*—It is considered by the author that the numerous cases in which chemical and mechanical influences, acting together, produce more damage than the sum of that produced by the two influences acting separately may be explained by the fact that the mechanical influence (whether alternating bending, abrasion or impingement of vacuum cavities) keeps removing the corrosion product which otherwise would slow down the attack, so that the chemical process continues at its high original velocity. He has put forward this view<sup>2</sup> in connection with a discussion on cavitation—a matter of practical importance in marine and hydro-electric engineering.

<sup>1</sup> To facilitate the application of the t-test, special curves have been plotted by Thornhill. See U. R. Evans, *Engineering*, 1943, vol. 156, p. 295.

<sup>2</sup> U. R. Evans, *Engineering*, 1943, vol. 155, p. 494. The theory has much in common with that put forward in an early paper by G. D. Bengough and R. May, *Engineer*, 1923, vol. 136, p. 7.

## IV.—OXIDATION, TARNISHING AND FILM-GROWTH.

(a) *General.*—In 1935 there was disagreement regarding even the order of magnitude of the rate of oxidation which occurred when freshly abraded metal was exposed to dry air at the ordinary temperature. There were also very big differences between values published for film thicknesses needed to cause the various colours observed on heated iron or copper. It seemed that the development of an electrometric method of measuring oxide films, similar to that used by Bannister<sup>1</sup> in early work at Cambridge as an auxiliary method in estimating silver iodide films, might be useful in obtaining a decision on both points. This led to Miley's work on oxide films, described below.

A rule generally observed in the Cambridge Corrosion Laboratory has been that, before any method is used for measuring film thicknesses, it should be compared with one or more other methods; also that, whenever possible, the measurements based on different methods should be carried out on the *same* specimen (thus avoiding complications due to the fact that two specimens treated in the same way do not always develop films of the same thickness). For instance, before the research on the growth of silver iodide films mentioned above, Bannister took silver specimens, exposed them to iodine, noting the weight increase, reduced the iodide cathodically, noting the coulombs required, and finally estimated the soluble iodine which had passed into solution. He thus obtained three independent measurements from *each* specimen. A number of specimens were tested and the agreement obtained within the sets of three values gave confidence in the results. It consequently became possible to use whichever of the three methods appeared most convenient when working out thickness-time curves and the effects of different factors on film growth.

Similarly, Price and Thomas,<sup>2</sup> in studying sulphide films, first measured the weight increment when the film was produced, next the number of coulombs needed for its reduction, and finally the

TABLE I.—*Comparison between Measurements of Silver Sulphide Films by Three Methods on Each Specimen.*

Specimen No.	Gain in Weight. Mg.	Electrometric. Mg.	Loss in Weight. Mg.
I.	3.60	3.61	3.46
II.	3.93	3.81	3.83
III.	4.80	4.90	4.60
IV.	3.93	4.02	3.86

<sup>1</sup> U. R. Evans and L. C. Bannister, *Proceedings of the Royal Society*, 1929, A., vol. 125, p. 378.

<sup>2</sup> L. E. Price and G. J. Thomas, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 332.

weight loss accompanying that reduction. Here, again, the three measurements obtained from each specimen (*see* Table I.) stood in satisfactory agreement.

(b) *The Electrometric Method as Applied to Oxide Films.*—In Miley's procedure<sup>1</sup> a specimen of iron or copper, superficially oxidised by previous heating, is made the cathode in an electrolytic cell containing ammonium chloride solution, a constant current being supplied from a high e.m.f. through a high series resistance, so that any small changes of polarisation and resistance during the process do not affect constancy. A voltmeter placed in parallel with the cell shows a change when the reduction of oxide is complete, since thereafter the current is employed in another reaction (liberation of hydrogen) which requires a greater depression of the cathodic potential; this change indicates the end-point. The coulombs which have passed give, by Faraday's law, the amount of oxide, and by dividing the oxide per unit area by the density the thickness—as defined by the mean of the intercepts made between the outer and inner surfaces of the film by lines drawn normal to the *general* plane of the specimen—is obtained. A knowledge of the oxide and its reduction product is, of course, needed. Cuprous oxide films were reduced to metallic copper, and ferric oxide films to ferrous oxide, which is soluble in ammonium chloride.

The checking of the electrometric method against other methods has presented more difficulty in the case of oxide films than in that of iodide films or sulphide films. The weight increase produced by heating was measured, but this was not a measure of the total oxide, since some oxide was always present at the first weighing. Accordingly the low-temperature oxide was estimated by electrometric study of unheated specimens, and added on. This furnished measurements showing a parallelism to the purely electrometric estimations, although the "corrected gravimetric" results were always about 60 Å. lower.<sup>2</sup> It will be noticed, however, that the "corrected gravimetric" results were really in part gravimetric and in part electrometric, and that in this procedure the principle of independent measurements on a single specimen was not observed. It was decided later to subject the oxide to *incomplete* cathodic reduction and to note the accompanying weight loss. This furnished a comparison of a purely gravimetric with a purely electrometric value, both obtained from a single specimen, and excellent agreement was obtained between the pairs of values,<sup>3</sup> thus confirming the view that the reduction was from ferric to ferrous oxide.

(c) *Thicknesses Corresponding to Various Interference Colours.*—Miley tinted specimens of iron and copper to give various inter-

<sup>1</sup> H. A. Miley, *The Iron and Steel Institute, Carnegie Scholarship Memoirs*, 1936, vol. 25, p. 200.

<sup>2</sup> U. R. Evans and H. A. Miley, *Nature*, 1937, vol. 139, p. 283.

<sup>3</sup> H. A. Miley and U. R. Evans, *Journal of the Chemical Society*, 1937, p. 1298.

ference colours, and estimated the thicknesses electrometrically, obtaining the results shown in Table II.

TABLE II.—*Electrometric Estimates of Film Thickness.*

Oxide Films on Iron.		Oxide Films on Copper.	
Colour.	Thickness. Å.	Colour.	Thickness. Å.
Straw yellow . .	440	Dark brown . .	370
Reddish yellow . .	530	Red brown . .	410
Red brown . .	560	Purple . . .	460
Purple . . .	625	Violet . . .	485
Violet . . .	695	Blue . . .	520
Blue . . .	725	Silvery green . . .	800
		Yellow . . .	940
		Orange . . .	1170
		Red . . .	1240

Before comparing Miley's results with those obtained elsewhere it must be pointed out that colour does not in itself fix the amount of oxide present. Vernon, Wormwell and Nurse<sup>1</sup> (at Teddington) have proved that two specimens may show the same colour (of the same order) and yet carry different amounts of oxide if their previous history has been different. Again, it must be remembered that the different methods of assessing "thickness" do not really measure the same thing. The gravimetric method gives the difference between the oxide present on the occasions of the first and second weighings; that present at the time of the first weighing may not be negligible. The optical method gives the effective distance between two reflecting surfaces, which may be uneven and diffuse. The electrometric method gives the whole of the *reducible* oxygen accessible to cathodic treatment; if the specimen has not been subjected to vacuum treatment, this may include adsorbed oxygen. Evidently there is no reason to expect exact agreement between results obtained in different laboratories, or even by different methods in one laboratory, although the order of magnitude should be the same.

Miley's electrometric results for oxide films on iron and copper agree, usually within 20 Å., with the early optical measurements of Constable.<sup>2</sup> Later experiments by Campbell and Thomas<sup>3</sup> (at New York), using an electrometric method based on that of Miley

<sup>1</sup> W. H. J. Vernon, F. Wormwell and T. J. Nurse, *Journal of the Chemical Society*, 1939, p. 628. In earlier work W. H. J. Vernon (*Transactions of the Faraday Society*, 1935, vol. 31, p. 1670) had shown that the absence of interference colours is no criterion of the thinness of a film.

<sup>2</sup> F. H. Constable, *Proceedings of the Royal Society*, 1927–28, A., vol. 117, pp. 385, 386.

<sup>3</sup> W. E. Campbell and U. B. Thomas, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 303.

but embodying (in the author's opinion) considerable improvements, gave results for films on copper lower than those shown in Table II. Analyses by Vernon, Wormwell and Nurse of the stripped films from iron tinted to two colours also gave numbers lower than those of Miley, whilst Miley's own "corrected gravimetric" results are consistently lower than his electrometric values. Winterbottom<sup>1</sup> has suggested that each of these methods is subject to a zero error, and that agreement between any two sets of thicknesses merely means that the zero error for the two procedures happened to be the same. Whilst some doubts regarding the absolute thickness still remain, all the tables recently produced show numbers of the same order of magnitude, and agreement is much closer than was the case eight years ago.

(d) *Time-Thickness Curves.*—The possibility of a constant zero error will not affect velocity measurements or the shape of time-

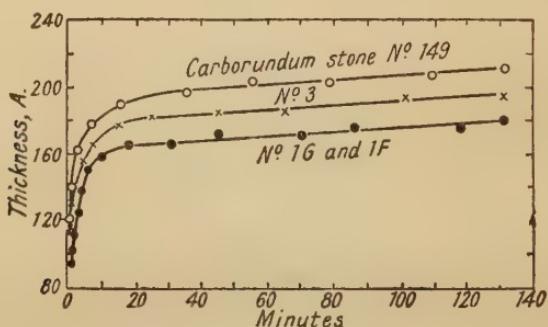


FIG. 7.—Curves obtained by Electrometric Method showing the Growth of Invisible Oxide on Iron Exposed to Dry Air at 18° C.; the three curves refer to different surface finishes (from *Journal of the Chemical Society*, 1937, p. 1296, Fig. 1).

thickness curves obtained electrometrically. Miley<sup>2</sup> traced numerous curves for iron exposed to air at various temperatures between 18° and 355° C. Those showing the growth of invisible oxide on iron in dry air at 18° C. are reproduced in Fig. 7 for three surface roughnesses. The oxidation proceeds rapidly in the first few minutes, becoming slow after about half an hour. The same is true of copper<sup>3</sup> exposed to dry air at 18° C.

After returning to America, Miley<sup>4</sup> traced oxidation curves on copper at a variety of temperatures; later, in collaboration with

<sup>1</sup> A. B. Winterbottom, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 326.

<sup>2</sup> H. A. Miley and U. R. Evans, *Journal of the Chemical Society*, 1937, p. 1295.

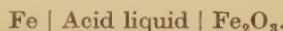
<sup>3</sup> U. R. Evans and H. A. Miley, *Nature*, 1937, vol. 139, p. 283.

<sup>4</sup> H. A. Miley, *Journal of the American Chemical Society*, 1937, vol. 59, p. 2626.

Cruzan,<sup>1</sup> he studied the conditions under which a layer of cupric oxide appears upon that of cuprous oxide.

(e) *Electrometric Estimation of Tarnish Products on Silver and Copper Alloys.*—One advantage of the electrometric method is that the different constituents of a film are reduced at different potentials, and can thus be estimated separately. Cruzan and Miley's work on films containing both cuprous and cupric oxides, just mentioned, furnishes a simple example. The film present on tarnished silver-copper alloys may contain four compounds, cuprous oxide, cuprous sulphide, silver sulphide and silver sulphate. Price and Thomas<sup>2</sup> have used Miley's electrometric procedure for detecting, and in some cases estimating, all four bodies in the presence of one another.

(f) *Transfer of Films to Transparent Supports.*—Much information may be obtained by moving oxide films from the metal to a plastic basis like celluloid. The oxidised face of a metal sheet is cemented to celluloid and the metal anodically dissolved from the back, leaving its oxide film on the plastic. It is necessary to steer between two dangers. If a neutral solution is used, it is likely to contaminate the films with ferric hydroxide, produced by hydrolysis of the iron salts. As pointed out in connection with the early film-stripping process using aqueous iodine,<sup>3</sup> this contamination can be largely removed by washing with dilute hydrochloric acid, but it is well to avoid it altogether. By ensuring against oxidation to the ferric state, and by using a faintly acid liquid, hydrolysis and contamination can be avoided, but such a liquid is apt to destroy the film, as a result of the local cell :



The ferric oxide, being the cathode of the cell, will be reduced to ferrous oxide, which will dissolve in the acid liquid; the direct solvent action of acid on ferric oxide is very slow. This destruction of film matter can be avoided if at all junctions between ferric oxide and iron the anodic polarisation is so high as to prevent the ferric oxide from acting as the cathode in a local cell. By using a cell of appropriate geometrical design, the author<sup>4</sup> has transferred, to celluloid, films of all thicknesses down to the lower limit of interference colours. The problem becomes increasingly difficult as the film becomes thinner and interlocking more pronounced. The method in its present form is not well suited for the transfer of invisible oxide, but it is hoped to overcome the difficulties later.

<sup>1</sup> C. G. Cruzan and H. A. Miley, *Journal of Applied Physics*, 1940, vol. 11, p. 631.

<sup>2</sup> L. E. Price and G. J. Thomas, *Transactions of the Electrochemical Society*, 1939, vol. 76, p. 329.

<sup>3</sup> U. R. Evans, *Journal of the Chemical Society*, 1927, p. 1025. In the alcoholic iodine method of W. H. J. Vernon, F. Wormwell and T. J. Nurse (*Journal of the Chemical Society*, 1939, p. 623) this contamination was avoided.

<sup>4</sup> U. R. Evans, Fifth Report of the Corrosion Committee, *The Iron and Steel Institute*, 1938, *Special Report No. 21*, p. 225.

Films have similarly been transferred to celluloid (also to black backgrounds) from tinted nickel, which displays much brighter colours than iron, both before and after transfer.

Optical theory indicates that if the films are single the colours after transfer should be complementary to those seen before transfer. The facts set forth in Table III. show that, on the whole, this

TABLE III.—*Colours of Films on Metal and after Removal to Celluloid.*

The Roman numeral indicates the "order."

Nickel Oxide Films.		Iron Oxide Films.	
Colour on Metal.	Colour after Transfer.	Colour on Metal.	Colour after Transfer.
Yellow I. Mauve I.	Bluish-white Whitish	Yellow-brown I. Mauve or violet I.	Bluish silver * Silvery grey * (some- times greenish)
Blue I. " Silvery hiatus "	Yellow Red	Full blue I. Pale blue I.	Gold yellow * Reddish *
Yellow II. Red II. Blue II. Green II. Red III.	Mauve to blue Green Yellow Red Green	Reddish-blue II. Blue II. Greenish-blue II.	Reddish-blue † Blue † Greenish-blue †

\* Best seen from back.

† Visible from front, through celluloid. Back view shows only the under layer of opaque magnetite.

complementary relationship obtains for nickel oxide films of all thicknesses, and probably for the thinner films on iron, although the tints after transfer are here very weak. The thicker films on iron have the same appearance before and after transfer, because here an opaque layer of magnetite exists below the ferric oxide. When viewed through the celluloid, the colour is the same whether or not the iron basis has been dissolved away, since in either case the true reflecting surface is magnetite. When viewed from the "back," the thicker films show no colours at all, apart from the bluish-grey of the opaque magnetite, whereas the thinner films, where there is no layer of magnetite, display their colours best when viewed from the back.

In the course of this research, evidence was collected which showed that in the case of the thinner films the oxide was much interlocked with the metal. Clearly, interlocking will affect the protective character of films. It was noticed in early work<sup>1</sup> on iron and copper that films producing definite interference tints

<sup>1</sup> U. R. Evans, *Journal of the Chemical Society*, 1925, p. 2191; 1927, p. 1028.

afforded less protection than those just insufficient, or barely sufficient, to give colour. Later this was confirmed<sup>1</sup> by measuring the amount of nitric acid which must be added to copper nitrate solution before it could act upon superficially oxidised iron—a quantitative, if somewhat arbitrary, method of expressing the protective power of a film. The relatively high degree of protection from films just short of the interference-colour range appeared to be largely due to interlocking.

Transfers of oxide films from molten metals to glass or mica can be made by hand. In early work<sup>2</sup> the author had studied the interference colours on lead before and after transfer, and in 1936 Miley<sup>3</sup> made similar transfers of films from tin, zinc and bismuth, all of which show bright colours.

(g) *Theoretical Derivation of the Growth Laws.*—As a result of work in a number of laboratories, three equations of growth are now established :

The linear law

$$y = k_1 t$$

The parabolic law

$$y^2 = k_2 t + k_3$$

The logarithmic law

$$y = k_4 \log (k_5 t + k_6)$$

where  $y$  is the film thickness at time  $t$ , and  $k_1, k_2, k_3, k_4, k_5$  and  $k_6$  are constants.

It is generally agreed that the linear equation is obeyed when definite cracks or voids pass through the greater part of the film. Probably the rate of oxidation is controlled by passage through a layer of constant thickness next to the metal which is of a more compact character, so that the thickness of the outer (cracked) portion does not affect the rate of oxidation. The author<sup>4</sup> has extended this notion of a double film (for which Vernon's observations at Teddington provide experimental evidence) to account for the logarithmic growth law also.

Provided that a fissure passing through the outer portion of a film is uninterrupted, the rate of passage through it will not be affected by its length, i.e., by the thickness of the film, since the rate will be controlled by the compact portion near the metal. Nevertheless, the prospects of a given fissure passing right through the film without becoming blocked will be affected by its length, i.e., by the film thickness. If the probability of blockage is appreciable, the transport through unit area of film will become proportional to the fraction of the fissures which penetrate completely. If we denote by  $p$ .  $dy$  the chance of an obstruction occurring in the

<sup>1</sup> U. R. Evans, *Journal of The Iron and Steel Institute*, 1940, No. I., p. 226 P.

<sup>2</sup> U. R. Evans, *Proceedings of the Royal Society*, 1925, A., vol. 107, p. 232.

<sup>3</sup> H. A. Miley and U. R. Evans, *Chemistry and Industry*, 1936, vol. 14, Jan. 10, p. 31.

<sup>4</sup> U. R. Evans, *Transactions of the Electrochemical Society*, 1943, vol. 83, p. 335. The line of thought owes much to suggestions embodied in papers or correspondence by W. H. J. Vernon, L. Tronstad, J. S. Dunn, F. J. Wilkins and others.

portion of the fissure contained in a film element of thickness  $dy$ , then the chance that a given fissure will penetrate without obstruction a film of finite thickness  $y$  must be  $e^{-py}$ , provided that  $p$  is the same in all layers of the film. We can then at once write the growth law as :

$$\frac{dy}{dt} = Ke^{-py}$$

or

$$y = \frac{1}{p} \log_e (Kpt + Cp),$$

where  $K$  and  $C$  are constants. Writing  $k_4$  for  $1/p$ ,  $k_5$  for  $Kp$  and  $k_6$  for  $Cp$ , we arrive at :

$$y = k_4 \log_e (k_5 t + k_6)$$

—the logarithmic equation.

The parabolic equation has also been the subject of theoretical study at Cambridge. Clearly, if, instead of a finite number of large fissures, the film-substance is *per se* permeable, almost *any* mechanism of transport through it will lead to :

$$\frac{dy}{dt} = K/y \quad \text{or} \quad y_2 = k_2 t + k_3$$

where  $k_2$  represents  $2K$ . But in order to explain the value of the constant  $k_2$  the cause of the permeability must be known; since the experimental values of  $k_2$  for different metals are of different orders of magnitude, a theoretical interpretation is urgently called for. Actually most of the films which freely permit growth in the absence of discrete fissures are those containing blank spaces in the cation lattice. The passage of metal outwards is possible through such films, since into any blank space a neighbouring cation may move, leaving a new blank space which another cation may fill, and so on. This provides a mechanism for the metal moving outwards to meet the oxygen, leading to a continuous thickening of the film. It should be noted that passage of electrons outwards must keep pace with that of the cations if we are to avoid an accumulation of electric charge. Actually this movement of electrons is quite possible. A film of "nominally" cuprous oxide containing spaces in the cation lattice must contain cupric as well as cuprous ions (otherwise there would be an excess negative charge), and electrons can be passed along between cupric and cuprous ions. Hoar and Price<sup>1</sup> pointed out that this dual movement of ions and electrons makes the situation analogous to the generation of current by a primary cell short-circuited by a copper wire, where the movement of cations and anions towards the two electrodes can be regarded as alternative (or parallel) paths, but the movement of electrons through the external wire proceeds along a series path, and must keep pace exactly with the ionic movement. Arguing in this way, they showed that Wagner's

<sup>1</sup> T. P. Hoar and L. E. Price, *Transactions of the Faraday Society*, 1938, vol. 34, p. 867.

equations for the dependence of the velocity constant on the e.m.f. of the cell metal|oxygen, the electrical conductivity of the film substance and the transport numbers can be derived immediately from the laws of Ohm and Faraday. Price<sup>1</sup> has compared the values of the velocity constant  $k_2$  thus calculated with the experimental values in those cases where the electrical data are available; the agreement is satisfactory.

(h) *Prevention of Oxidation and Tarnishing by Pretreatment.*—Price and Thomas<sup>2</sup> have used the principles just set forth to interpret their own researches into the effect of various additions to silver on its tarnish resistance and also the results of Fröhlich<sup>3</sup> on the oxidation of various copper alloys. Qualitatively, the principles seemed to offer a basis of interpretation, since additions of metals like aluminium or beryllium which form very badly conducting oxides are outstanding in increasing the resistance to oxidation and tarnishing. But when an attempt was made to compare the experimentally determined oxidation rate of a copper-aluminium alloy with that predicted by theory on the assumption that the film consisted of pure alumina, the numbers were of the wrong order of magnitude. They concluded that the film did not consist of pure alumina, but of alumina containing copper oxide in solid solution, and that far better resistance could be obtained by commencing oxidation under conditions leading to pure alumina. In this way was developed the method known as *selective oxidation*, which consisted in heating the copper-aluminium alloy at 800° C. in a hydrogen atmosphere containing water vapour at a partial pressure of 0·1 mm. of mercury. Such a treatment could not possibly oxidise copper, but the aluminium, with its far greater affinity for oxygen, was appreciably oxidised, although the alumina film produced no alteration in appearance. After this treatment it was possible to heat the alloy strongly in oxygen, and it remained bright under circumstances which caused the untreated alloy to be rapidly darkened. Quantitative measurements indicated that the oxidation rate was now of the order of magnitude predicted from theory on the assumption that the film was pure alumina.

A similar pretreatment was also employed by Price and Thomas in developing a form of silver resistant to tarnishing by a sulphurous atmosphere which blackens ordinary silver. The alloy used for the selective oxidation contains aluminium or beryllium, but conforms to the definition of standard silver. Selective oxidation cannot be used directly to prevent the tarnishing of silver articles made of the ordinary silver-copper alloys, but an alternative method of depositing a film of beryllia by electrochemical means on such

<sup>1</sup> L. E. Price, *Chemistry and Industry*, 1937, vol. 15, Aug. 28, p. 769.

<sup>2</sup> L. E. Price and G. J. Thomas, *Journal of the Institute of Metals*, 1938, vol. 63, pp. 21, 29; 1939, vol. 65, p. 247.

G. J. Thomas and L. E. Price, *Metal Industry*, 1939, vol. 54, p. 189.

<sup>3</sup> K. W. Fröhlich, *Zeitschrift für Metallkunde*, 1936, vol. 28, p. 368.

articles was worked out, and this gave considerable resistance to tarnishing.

Despite the apparently academic arguments which led to its discovery, the principle of selective oxidation appears to have many practical applications. It may be possible, after the end of the war, to apply it to increase the resistance of ferrous materials.

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#### CORRESPONDENCE.

Dr. W. H. J. VERNON and Dr. F. WORMWELL (Chemical Research Laboratory, Department of Scientific and Industrial Research, Teddington) wrote: This paper by Dr. Evans constitutes an impressive and most valuable document, on which we would offer our sincere congratulations. Covering as it does such an extraordinarily wide range of activities, systematic discussion is difficult; we propose, therefore, to confine our remarks to some of those aspects which bear on work carried out at the Chemical Research Laboratory, Teddington, to which Dr. Evans has so kindly referred, since we may thereby be the better able to bring out points of immediate mutual interest.

The outstanding contributions made by Dr. Evans and his collaborators in demonstrating the electrochemical mechanism of wet corrosion processes, as summarised in Section II., have in general been concerned with conditions (*e.g.*, of partial immersion) such that corroding and protected areas are well defined and spatially separated. On the other hand, the Teddington work has been concerned mainly with totally immersed metals, on which the distribution of corrosion is not always so regular. Corrosion rates have been measured by determinations of oxygen absorption, hydrogen evolution, loss of weight, penetration of corrosion and analysis of corrosion products. Although direct electrochemical measurements have formed but a minor part of the published investigations, it is considered that the quantitative data obtained are, in general, quite consistent with the electrochemical mechanism of corrosion as now widely accepted. A review of the fundamental researches of G. D. Bengough and his colleagues from this point of view was contemplated before the war, but this, along with the researches themselves, has been suspended on account of pressure of war problems.<sup>1</sup>

A series of electrochemical investigations was commenced at the Chemical Research Laboratory in 1939, but was suspended before any results had been reported. Although the technique

<sup>1</sup> The Teddington work on atmospheric corrosion (also interrupted by the war) has recently been summarised by one of the writers (Jubilee Memorial Lecture to the Society of Chemical Industry, *Chemistry and Industry*, 1943, vol. 62, p. 314).

was not developed sufficiently to determine equipotential lines in the manner so elegantly developed by Dr. Agar at Cambridge, it may be of interest to summarise the preliminary results. Using a mild-steel disc totally immersed in  $N/1000$  NaCl at a depth of 1.5 cm., a potential drop of about 100 millivolts was measured between points in the solution close to the upper (corroding) face and the under (protected) face of the disc. This value was observed after 4 days' immersion, when the characteristic distribution of corrosion in these conditions had been attained. At 100 days, the corresponding potential drop was about 70 millivolts. It is significant that previous work had shown that the corrosion rate becomes less after a period varying between about 20 and 50 days. It seems clear that the corrosion is associated, at least in part, with currents flowing from corroded (anodic) to protected (cathodic) areas in conditions of complete immersion. Earlier work<sup>1</sup> had shown that after long periods the whole surface of a specimen often becomes corroded and may indeed be completely embedded in a mass of corrosion product. The identification of anodes and cathodes is then much more difficult, but there is no reason to doubt that the corrosion process is still electrochemical. A possibility discussed at Teddington is that the magnetite layer of corrosion products, which forms on the metal surface and becomes hard after long periods, may function as the cathode surface in the later stages.

The work on inhibitors described by Dr. Evans is of the greatest interest and brings out very clearly points that should be carefully observed by all those who wish to make use of this method of suppressing corrosion under immersed conditions. The present position appears to be that "safe and efficient" treatment is still difficult in cooling systems utilising comparatively fresh waters. Much intensive work has been carried out at Teddington on the inhibition of corrosion in cooling systems using solutions high in chlorides or other corrosive salts. In general, chromates appear to be among the most effective inhibitors, but, as in Dr. Evans' work, they cannot be classed as entirely "safe." In fact, treatment with chromate or other inhibitors has often appeared very promising in preliminary tests, but has led to very severe pitting in longer-time laboratory tests and in service conditions. Confirming the work with Dr. Thornhill, referred to by Dr. Evans on p. 82 P, it was found that an important factor is the passage of heat through metal walls into the cooling water. This may result in failure of inhibition, which is not revealed in a test where heat is applied through glass to a solution containing separate metal specimens.

The Cambridge work on causes of blistering in paints should lead to valuable advances. If the mechanism now outlined by

<sup>1</sup> G. D. Bengough, A. R. Lee and F. Wormwell, *Proceedings of the Royal Society*, 1931, A., vol. 134, p. 336. G. D. Bengough and F. Wormwell, Third Report of the Corrosion Committee, p. 138, *The Iron and Steel Institute*, 1935, *Special Report No. 8*.

Dr. Evans is of general application, it would imply that appreciable corrosion at some point on a metal specimen is necessary to produce anodic products and cathodic alkali, respectively, at the places where the two types of blister (referred to by Dr. Evans) are formed. No doubt, blistering of these types does occur according to this mechanism. On the other hand, extensive investigations (unpublished) at Teddington have revealed rather different phenomena. In conditions of rapid movement of painted steel specimens in sea water (natural or synthetic) small blisters usually appear before there is any visible sign of corrosion anywhere on the specimen. When a blister breaks, the steel beneath is at first bright and uncorroded, remaining so for one or two days and then beginning to rust. It has not been possible to obtain definite indications of the *pH* value inside the blisters in these tests, which included many ships' bottom compositions and other anti-corrosive paints. Recently, however, using painted steel sheets partially immersed in stagnant sea water in the laboratory, the following observations have been made. Immediately after removal from the sea water, small blisters have been opened with a pen-knife, revealing bright steel beneath. There was apparently no liquid inside the blisters, but filter-paper strips soaked with Universal indicator gave alkaline (*pH* about 11) or acid (*pH* 4-5) reactions at the surface of the steel. The acid reaction was obtained only at points contiguous with rust spots, but the blisters were clearly not produced directly by either ferrous salts or rust. The development of alkali is therefore not an essential factor in the production of blisters. The presence of salt in the water, although not essential, does appear to accelerate very greatly the formation of blisters and the flaking of paint. Comparative tests (under conditions of rapid movement) of several types of bituminous and coal-tar paints in distilled water and sea water have shown good results for 50 days as compared with breakdown in 2-3 days, respectively. Further work is contemplated on the effect of water and of different salts on the stability and strength of paint films. The effect of hydrogen gas evolution in sea water, as suggested by Bengough and Lee,<sup>1</sup> should not be overlooked. "Ageing" effects due to physical and chemical processes within the paint matrix must also contribute to the formation of blisters and other defects. The Teddington work (and indeed the experience of paint technologists and paint users) bears out Dr. Mayne's observation of blister formation in the absence of zinc. Such changes are generally recognised to be one of the chief causes of failure in underwater paints.

The development by Dr. Evans of cementiferous paints is of outstanding importance, and such paints are likely to play an increasingly valuable part in underwater protection. So far as rapidly moving conditions are concerned, the writers can testify to the promising behaviour of a single-coat application (on mild

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1932, No. I., p. 299.

steel) of a cementiferous paint, kindly supplied by Dr. Evans, when submitted to the severely accelerated test conditions of the "C.R.L. rotor apparatus."

Dr. Evans refers (Section IV.(a)) to his demonstration that in salt solutions a much higher current density is needed for cathodic protection under moving than under stagnant conditions. In unpublished work at Teddington using zinc connected to steel in sea water it has been found that a higher current density is automatically supplied by the zinc in moving conditions, owing to rapid replenishment at the steel surface of dissolved oxygen (the main cathodic stimulator). Replenishment of calcium and magnesium salts may also play a part. Deposits of calcium and magnesium compounds on the cathode surface have been shown, in the Teddington work, to play an important rôle in the maintenance of protection. This factor does not always receive sufficient emphasis in discussions of the theory of cathodic protection.

Turning to the final Section on oxidation and film growth, we should like to pay tribute to the great value of the Cambridge work in this field and to its stimulating influence on work in other laboratories. With regard to values of film thickness, on which there was much discussion a few years ago, Dr. Evans has rightly emphasised the much greater degree of agreement that now obtains among various methods by various workers; he has also usefully pointed out that some of the differences must be genuine, since different methods of assessing "thickness" do not really measure the same thing. In particular, it is not surprising that the electro-metric method, so ably developed by Dr. Miley, should tend to give the highest values, because, as Dr. Evans points out, it takes account of the whole of the reducible oxygen accessible to cathodic treatment. With regard to gravimetric methods, we agree that the film on the metal before the first weighing is not always negligible. It is of interest to note, however, in the case of visible films on iron produced by heating in air, that some special significance does attach to that part of the film measurable by weight increment alone. Although the evidence indicated that the underlying "primary" film (probably an aggregate of ferric oxide and metallic iron) plays an essential part in the optical effects arising from subsequent film formation, it was found<sup>1</sup> that the film stripped from specimens heated to the first-order straw colour coincided with that measured by the increase in weight of the specimen. Until recently there has been a tendency to regard thickness values obtained by Constable's optical method as being particularly free from qualification. In spite of the extreme experimental accuracy achieved it is evident that this view is unjustified, since the "thickness" so derived must depend ultimately on the value assumed for the refractive index. The substitution of a not unreasonable alterna-

<sup>1</sup> W. H. J. Vernon, F. Wormwell and T. J. Nurse, *Journal of the Chemical Society*, 1939, p. 621.

tive for the refractive index<sup>1</sup> employed by Constable would bring his thickness values for all colours much nearer to those obtained by some other methods.

Dr. Evans' theoretical derivation of the logarithmic law has proved a valuable adjunct in interpreting some of the Teddington work on direct oxidation. The principle of selective oxidation, as developed by Price and Thomas, is likewise a most helpful conception. It is being used to interpret certain results, which we hope shortly to publish, arising from a study of the surface film on 18/8 chromium-nickel stainless steel. (Much of this work had been completed before the war, but has since been in abeyance.) We entirely agree with Dr. Evans as to the important part which this principle will almost certainly play in further developments in the field of metallic oxidation.

We should like to add that the recent work at Teddington referred to in this contribution has been carried out with the able assistance of Messrs. T. J. Nurse, E. G. Stroud, H. C. K. Ison and J. A. Lewis. References to unpublished work have been included with the approval of the Department of Scientific and Industrial Research.

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#### AUTHOR'S REPLY.

The AUTHOR wrote in reply : The kind words of Dr. Vernon and Dr. Wormwell are most welcome, and will be a real encouragement to all those working at Cambridge. Their outline of recent results at Teddington will arouse general interest. Particularly it is satisfactory to find that results obtained before the war had already indicated the existence of considerable potential differences between the upper and lower faces of a corroding disc. This would seem to indicate that on horizontal specimens, just as on vertical specimens, there exist in the early stages large anodic and cathodic areas. It will be interesting to learn the electrochemical distribution of anodes and cathodes in the later stages, when the whole surface has become corroded. The suggestion that the magnetite layer functions as cathode appears reasonable. It is hoped that the time is not too distant when Dr. Vernon and Dr. Wormwell, with their colleagues, may take up this research again.

An account of the experience on blistering obtained at Teddington is also welcome. It seems at least possible that there is more than one way in which blisters can be formed, and this makes the practical problem of avoiding them all the more difficult. Clearly, any blister which appears at a time when the steel is completely uncorroded must have been formed in some way other than that

<sup>1</sup> This refractive index, published by Kundt many years earlier, had been obtained on a sample of iron oxide by no means necessarily identical in composition and properties with the thin surface films examined *in situ* by Constable (Vernon, Wormwell and Nurse, *loc. cit.*, p. 630).

described in the author's paper. On the other hand, the theory emerging from Dr. Mayne's observations at Cambridge does not necessarily call for a correlation between the site of the blisters and the location of rust patches. If alkali and ferrous salts are formed close together, they will precipitate one another, producing a patch of rust, but, since both soluble bodies are destroyed, there is likely to be no loosening of the paint coat. Where they are formed far apart, there will be blisters at the cathodic points and rust-nodules at the anodic points, but rust will not appear below the paint at the blisters proper.

The amount of alkali needed to soften or loosen a paint coat is small. In early work on alkaline softening,<sup>1</sup> drops of  $N/2$  sodium chloride solution placed on steel coated with gold or bronze paint produced loosening of the coat around the periphery where alkali was formed, at a time when the centres of the drop areas, although showing visible anodic attack, still held fast the paint coat (doubtless the flaky form of the pigment particles allowed them to cling to the metal, even though some incipient pitting had set in at points covered by each flake).

Evidently more work will be needed before blistering is fully understood. It is believed that, as soon as the facts have been established, it should be possible to arrive at an agreed explanation of the different types of blister.

The statement by Dr. Vernon and Dr. Wormwell regarding the results of the tests on cementiferous paints carried out at Teddington is very encouraging. The author would like to express his thanks for the carrying out of these tests.

It is a matter of great satisfaction that the theoretical derivation of the logarithmic law has been helpful to the workers at Teddington. The publication of the work at Teddington on the stripping and composition of the surface film from stainless steel will arouse widespread interest, and it is hoped that, in the not too distant future, this extremely valuable line of research will be resumed at Teddington.

<sup>1</sup> U. R. Evans, *Transactions of the Electrochemical Society*, 1939, vol. 55, p. 257.



# SOME MEASUREMENTS OF CORROSION-FATIGUE MADE WITH A NEW FEEDING ARRANGEMENT.<sup>1</sup>

By A. U. HUDDLE, B.A., AND U. R. EVANS, Sc.D., M.A. (THE METALLURGICAL LABORATORIES, CAMBRIDGE UNIVERSITY).

*Paper No. 11/1943 of the Corrosion Committee.*

## SUMMARY.

A new method of feeding corrosive liquid to a steel rod rotating in a fatigue-testing machine provides a sharply-defined ring of liquid renewed from a wick which neither touches nor appreciably shields the steel surface. This has been used to study the loss of strength and elongation which occurs in a rod subjected to alternating stresses when wetted with sea water; the deterioration of mechanical properties does not become serious until half the corrosion-fatigue life has elapsed. Coating with a paint richly pigmented with zinc dust increases the life; this is, in general, partly due to electrochemical protection and partly to mechanical exclusion.

## I.—DESCRIPTION OF THE APPARATUS.

*Previous Work.*—Most investigators on corrosion-fatigue have used standard fatigue machines, fitting to them a mechanism for applying the corrosive fluid. Thus, McAdam<sup>2</sup> applied a stream of liquid so as to surround the entire stressed surface with a water film. Inglis and Lake<sup>3</sup> used a rapid drip-feed, and Binnie<sup>4</sup> a slower one. Gerard and Sutton<sup>5</sup> boxed their specimens into a chamber and injected a spray.

These arrangements were well suited to the experimenters' several purposes. They give, however, no well-defined margin to the wetted area, and, in view of the fact that corrosion is often unusually intense at or near a "water-line," a sharp dividing line between wet and dry portions may often be desirable. This is particularly the case if it is desired to study the effect of corrosion-

<sup>1</sup> Received June 7, 1943. This paper is published by authority of the Corrosion Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

<sup>2</sup> D. J. McAdam, *Chemical and Metallurgical Engineering*, 1921, vol. 25, p. 1081. *American Institute of Mining and Metallurgical Engineers*, 1931. *Technical Publication No. 417: Transactions of the American Institute of Mining and Metallurgical Engineers*, 1932, *Institute of Metals Division*, vol. 99, p. 282.

<sup>3</sup> N. P. Inglis and G. F. Lake, *Transactions of the Faraday Society*, 1931, vol. 27, p. 803.

<sup>4</sup> A. M. Binnie, *Engineering*, 1929, vol. 128, p. 190.

<sup>5</sup> I. J. Gerard and H. Sutton, *Journal of the Institute of Metals*, 1935, vol. 56, p. 33.

fatigue applied at some chosen spot on a uniformly stressed specimen.

Accordingly, at Cambridge attempts have been made to ensure a sharp dividing line. Gould<sup>1</sup> applied the corrosive liquid by means of a sling of cotton tape which passed under the rotating specimen just out of contact with it; the tape was kept wet by a drip-feed. Such an arrangement causes a rather large portion of the experimental area to be shielded from air, and it seemed that it might be a further improvement to apply the liquid by means of a wick which approached the metal at one point only. This led to the apparatus described in the present paper. A modification of the feed, in which the wick is replaced by a vertical glass rod, coated with wax except along a narrow line down which the liquid flows, is being used in this laboratory by Mr. M. Tchorabdji for wire tests on the Haigh-Robertson machine.

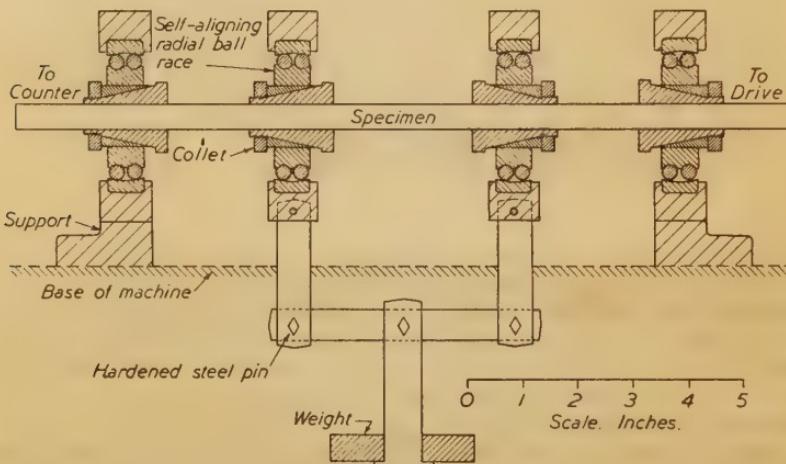


FIG. 1.—The Fatigue Testing Machine; the specimen, of uniform diameter, stressed uniformly between the two loading points.

*The New Apparatus.*—The fatigue machine used for this work tests a specimen of uniform diameter, loaded at two points, as shown in Fig. 1. As is well known, this gives a uniform stressing between the points of loading, and if the specimen is rotated every point on it is subjected to tension and compression alternately. Actually, two such machines were mounted on a single base, with a single drive. This is not an ideal arrangement, since the jerk caused by one specimen when it breaks may favour the failure of the other if it has already reached an advanced stage. A new machine is being designed at Cambridge to avoid this trouble.

<sup>1</sup> A. J. Gould, *Engineering*, 1933, vol. 136, p. 453. A. J. Gould and U. R. Evans, Second Report of the Alloy Steels Research Committee, p. 328, *The Iron and Steel Institute*, 1939, *Special Report No. 24*.

The feed is shown in Fig. 2. The wick, 3 in. long and  $\frac{1}{8}$  in. in dia., is held in a somewhat springy bow, made of vinyl resin, attached

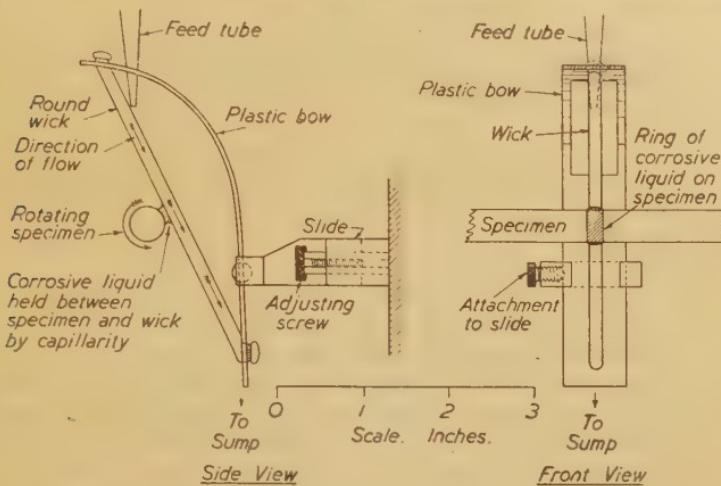


FIG. 2.—The Feed for the Corrosive Liquid.

to an adjustable slide. The corrosive liquid is fed to the top of the wick and flows down into a sump. The wick never touches the specimen, but liquid is held by capillarity between the wick and the metal; when the specimen rotates, a ring of corrosive solution, about  $\frac{3}{16}$  in. wide, passes right round the periphery, as shown in Fig. 3.

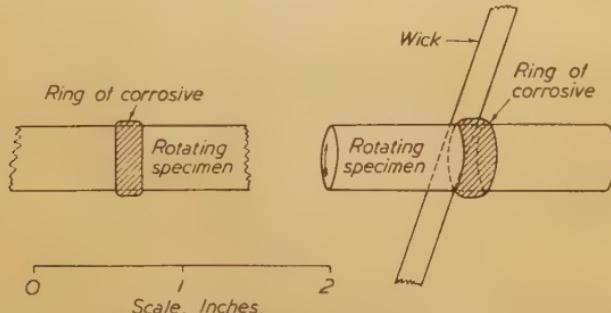


FIG. 3.—The Rotating Specimen surrounded by a Ring of Corrosive Liquid.

The machines were mounted in a basement room the temperature of which remained within  $2.5^{\circ}$  of  $17^{\circ}$  C. throughout the work. Gould's measurements of the temperature coefficient of corrosion-fatigue processes<sup>1</sup> indicate that the effect of such variation will be small compared with the variability of results due to other causes which, unfortunately, is usually experienced in corrosion-fatigue work.

<sup>1</sup> A. J. Gould, *Engineering*, 1936, vol. 141, p. 495.

*Applications.*—The apparatus has been used to obtain an answer to two important questions :

(i) When a metallic specimen is undergoing corrosion-fatigue, does its power to resist a steady stress deteriorate during early stages of the process, or can the strength be regarded as unchanged until shortly before the fatigue-failure sets in ?

(ii) Is it possible to restrain corrosion-fatigue damage by applying a paint containing zinc, even where, as will often happen in service, portions of the surface remain, or become, uncovered ?

Experiments to decide these questions were carried out on three steels, of which the analyses appear in Table I. The specimens of steels *C* and *D* were rods 0·45 in. dia. cut from  $\frac{5}{8}$ -in. ships' plates, by kind arrangement of Mr. V. G. Shepheard, the length of the specimen being parallel to the direction of rolling. These specimens were used as received, with a fine-ground finish. The specimens of *A* were prepared at Cambridge from black mild-steel rod of 0·5 in. in dia. These were finished to 0·45 in. with a fine grinding wheel, the surface being similar to that of the other specimens. The corrosive liquid was sea water from Portsmouth, kindly supplied by Dr. I. G. Slater. The frequency employed was 1335 r.p.m.

TABLE I.—*Analyses of the Steels Examined.*<sup>1</sup>

	Steel:	<i>A.</i>	<i>C.</i>	<i>D.</i>
Carbon. %	.	0·21	0·20	0·23
Silicon. %	:	0·20	0·03	0·08
Manganese. %	.	0·70	0·53	1·52
Sulphur. %	.	0·033	0·064	0·030
Phosphorus. %	:	0·023	0·032	0·020
Nickel. %	:	0·30	0·07	0·04
Chromium. %	:	0·06	0·04	0·02
Tungsten. %	:	...	...	...
Molybdenum. %	:	Trace	Trace	Trace
Vanadium. %	:	Nil	Nil	Nil
Copper. %	:	0·14	0·09	0·08

<sup>1</sup> Carried out at the Brown-Firth Research Laboratories through the kindness of Dr. W. H. Hatfield, F.R.S.

## II.—LOSS OF TENSILE STRENGTH DURING THE COURSE OF CORROSION-FATIGUE.

*Normal Life of the Materials in Sea Water.*—The life of the steels is shown in Table II. The agreement between different specimens is poor, but it is clear that steel *D* has a higher life than steel *C* at equal stress. Since, however, the tensile strength of *D* is 37·8 tons per sq. in. and that of *C* only 29 tons per sq. in., it would

seem fairer to compare the two materials at stresses representing the same fraction of the tensile strength, *i.e.*, to compare *C* at 7.6 tons per sq. in. with *D* at 10 tons per sq. in., or, alternatively, to compare *C* at 10 tons per sq. in. with *D* at 13.17 tons per sq. in. On this basis *C* is seen to be the more resistant to corrosion-fatigue. The life of steel *A* was measured only at 10 tons per sq. in., twelve experiments being performed on account of the high scatter.

TABLE II.—Corrosion-Fatigue Lives in Sea Water.  
Expressed in millions of cycles.

Steel.	Stress. Tons per sq. in.	Individual Lives.	Average.
<i>C</i>	± 10.0	1.26, 1.25, 1.54, 0.76, 0.96	1.15
<i>C</i>	± 7.6	3.34, 3.37, 2.34, 3.02	3.02
<i>D</i>	± 13.17	0.67, 0.61, 0.70, 0.62	0.65
<i>D</i>	± 10.0	1.85, 1.44, 1.76, 1.09	1.54
<i>A</i>	± 10.0	{ 1.66, 1.16, 1.95, 1.01, 1.60, 1.61, } { 1.51, 1.84, 1.81, 1.81, 2.09, 2.09 }	1.68

*Loss of Strength during Periods Insufficient for Breakage.*—The specimens were then subjected to corrosion-fatigue for periods representing different fractions of the average corrosion-fatigue life, and the tensile strength and elongation determined on a Macklow-Smith testing machine. The results are recorded in Table III.,

TABLE III.—Progress of Weakening during Corrosion-Fatigue in Sea Water.

Material and Stress.	Duration of Test as Percentage of Corrosion-Fatigue Life.	Tensile Strength as Percentage of Strength of Uncorroded Steel.	Elongation as Percentage of Elongation of Uncorroded Steel.
Steel <i>C</i> . ± 10 tons per sq. in.	33	100, 100, 100, 100	100, 100,* 100,* 100
	50	98, 98, 100, 100	95, 95, 95, 95
	67	85, 89, 92, 98, 98	65, 80, 75, 75, 85
	75	85, 57, 98	30, 0, 80
	85	95, 83	24, 10
Steel <i>D</i> . ± 10 tons per sq. in.	33	100, 99, 100, 100	100,* 100,* 100,* 100 *
	50	95, 99, 100, 99	35, 80, 100,* 80
	67	99, 86, 99, 73, 87	100,* 0, 40, 0, 20
Steel <i>C</i> . ± 7.6 tons per sq. in.	33	100, 100	100, 100
	52	100, 100	95, 100
	70	80, 80	16, 16
Steel <i>D</i> . ± 13.17 tons per sq. in.	33	100, 99, 100, 100	100,* 100,* 100,* 100 *
	50	100, 99, 99, 100	100,* 80, 80, 80
	67	100, 98, 99, 99	60, 60, 60, 60

\* Necked outside gauge-marks, *see text*.

the strengths and elongations being given, for convenience, as percentages of the average strength or elongation of the uncorroded material. Certain specimens marked with an asterisk "necked" outside the gauge lengths, and it was assumed that the corrosion-fatigue had then produced no deterioration of elongation at the point subjected to it. Even those specimens which had been subjected to corrosion-fatigue for only one-third of their lives contained small cracks, which revealed themselves during the subsequent tensile test.

*Conclusions.*—Up to about half the corrosion-fatigue life most of the specimens suffer little deterioration in tensile properties. Beyond half the average corrosion-fatigue life there is a fall in the breaking stress and a much larger drop in the elongation. This may be explained as follows: During the corrosion-fatigue period cracks are formed, reducing the tensile load needed to break the portion of the cross-section remaining uncracked. If this diminished breaking load is less than the yield point of the parts where there are no cracks, the specimen will fracture at the crack almost without elongation; but if it is greater, general deformation will occur, leading to work-hardening. When the resistance to deformation of the uncracked part of the specimen becomes equal to the maximum load which the partly cracked portion will withstand, fracture will occur at the cracks.

The fear that the straight tensile properties of material may begin to deteriorate long before there is danger of actual fracture through corrosion-fatigue is shown to be unfounded. On the other hand, the considerable variation of corrosion-fatigue life among "identical" specimens must be regarded as a matter of some concern.

### III.—INCREASE OF CORROSION-FATIGUE LIFE BY PAINTS CONTAINING METALLIC ZINC.

*General.*—Zinc paints may protect in two ways: (1) By excluding corrosive substances, (2) by cathodic protection at gaps in the coat. In service conditions gaps or porosity are liable to be present, at least when alternating stresses operate. The work of Stuart<sup>1</sup> indicates that contact with zinc may postpone the failure of uncovered steel under some conditions, and it would be convenient that the zinc should be applied as a paint coat.

For studying the electrochemical protection conferred by zinc, under conditions where mechanical exclusion of corrosive substances is incomplete, a number of inorganic paints were selected on account of their porous character; emulsion paints and polystyrene paints, now being developed in this laboratory by Dr. J. E. O. Mayne, were also included in the tests.

<sup>1</sup> N. Stuart and U. R. Evans, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 131 P.

*Experiments on Unpainted Specimens Joined Externally to Painted Strips.*—In order to study a case where mechanical protection was absent, unpainted specimens were used, but a strip of steel, coated with zinc-rich paint, was placed on the opposite side of a wick, as shown in Fig. 4, and joined electrically to the

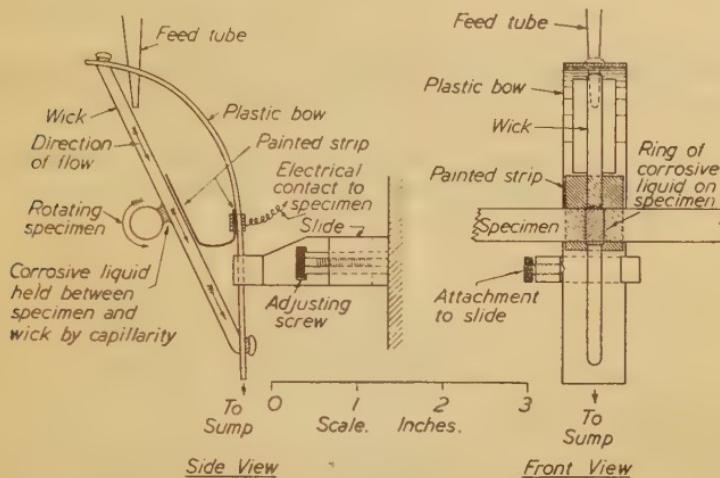


FIG. 4.—Modified Corrosive-Liquid Feeder for Tests on Paints containing Metallic Zinc.

specimen. Similar experiments were carried out using a strip of zinc sheet in the place of the zinc-painted steel. The results are shown in Table IV. It will be noticed that one of the paints

TABLE IV.—Corrosion-Fatigue Lives in Sea Water of Unpainted Specimens of Steel D Stressed at  $\pm 10$  tons per sq. in. in External Electrical Contact with Zinc or Zinc-Painted Steel Strip.

Contact Piece Used.	Individual Lives. Millions of Cycles.	Average.	
		Millions of Cycles.	Hours.
None . . . . .	1.85, 1.44, 1.76, 1.09	1.54	19
Pure zinc . . . . .	1.75, 3.95	2.85	36
Zinc-pigmented inorganic paint <i>E337/H</i> . . . . .	1.64, 2.80	2.22	28
Zinc-pigmented polystyrene paint . . . . .	1.97, 1.98	1.98	24
Zinc-pigmented emulsion paint.	1.72, 1.79	1.75	21

employed gives lives not very much shorter than those obtained by contact with pure zinc, and in all cases the average life exceeds the average obtained in the absence of zinc protectors. Comparing

the lives of the eight specimens joined to zinc or zinc paints with those of the four specimens not joined to zinc and applying the *t*-test,<sup>1</sup> it is found that the chance is less than 1 in 100 that such results would be obtained if junction with zinc was without benefit. The scatter makes it impossible to distinguish the relative merits of the different zinc paints; unfortunately, the number of specimens available was insufficient to carry out the experiments in sufficient multiple to place the paints in an order of merit.

*Experiments on Painted Specimens.*—In this series (Table V.) the specimen itself received a band of paint  $\frac{3}{4}$  in. wide; the wick

TABLE V.—Corrosion-Fatigue Lives in Sea Water of Painted Specimen of Steel A Stressed at  $\pm 10$  tons per sq. in.

Paint.	Individual Lives. Millions of Cycles.	Average.	
		Millions of Cycles.	Hours.
None . . . . .	Average of twelve (see Table II.)	1.68	21
Zinc-pigmented inorganic paints:			
E377/H . . . . .	3.88, 4.21	4.00	50
E378/H . . . . .	9.83, 4.96, 6.19, >10	>7.75	>98
E400 . . . . .	2.72, 2.94, 3.87, 4.97	3.62	47
E427 . . . . .	8.88, 5.50, 4.47	6.26	78
E475 . . . . .	7.30, 4.96, 4.41, 3.86	5.13	64
Zinc-pigmented polystyrene paint . . . . .	>10, 9.35, 7.83, 6.44	>8.40	>105
Zinc-pigmented emulsion paint . . . . .	2.96, 6.34, 8.16, 4.22	5.42	68
Iron-oxide-pigmented emul- sion paint . . . . .	2.77, 3.87, 2.44, 3.66	3.18	40
Zinc-pigmented chloro-rub- ber paint (commercial) .	>10, 7.93, 7.74, >10	>8.92	>112

was arranged to approach the metal on the band. Here the protection was partly electrochemical and partly mechanical. Thus, even an iron-oxide paint containing no zinc perceptibly raised the life, but it was inferior to all the paints containing zinc. Application of the *t*-test to the comparison of lives obtained with the zinc-pigmented emulsion paint and with similar paint pigmented with iron oxide showed that the odds were 11 to 1 against obtaining these results if the zinc paint was not genuinely superior. The longest lives were obtained with paints consisting of chlorinated rubber or synthetic resin richly pigmented with zinc dust, since here both forms of protection operated. Unfortunately, this class of paint tends to develop blisters in service, and experiments by

<sup>1</sup> See N. Stuart and U. R. Evans, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 143 p (Appendix II.). Also U. R. Evans, *Engineering*, 1943, vol. 156, p. 295.

Dr. J. E. O. Mayne are in progress at Cambridge to elucidate and overcome this blistering.

*Conclusions.*—Despite the scatter of the results, it is clear that paints containing zinc dust appreciably increase the corrosion-fatigue life of steel, whether they cover the whole of the steel surface or not. The longest lives are obtained when mechanical exclusion is present as well as chemical protection.

The authors desire to express their thanks for generous aid provided by The Iron and Steel Industrial Research Council through The Iron and Steel Institute Corrosion Committee, and especially to place on record their gratitude for the kind interest shown by the late Dr. W. H. Hatfield, F.R.S., Chairman of the latter body.

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#### CORRESPONDENCE.

Mr. D. J. MCADAM, jun. (National Bureau of Standards, Washington, U.S.A.) wrote : This paper is of considerable interest. As discussed by the writer in a number of papers, the corrosion-fatigue process may be followed by means of two-stage tests. In the first stage, the specimen is corroded under a chosen alternating stress; in the second stage the damage is evaluated by determining the fatigue limit by a test in air and comparing this fatigue limit with that of an uncorroded specimen. The same method has also been used by the writer to evaluate the damage due to stressless corrosion. The authors' use of a tension test to determine the damage due to corrosion for various lengths of time under alternating stress is of interest. It should be noted, however, that this method would give no indication of loss of resistance of a metal to repeated stresses. For steels in well water or salt water, damage as determined by fatigue test tends to be rapid at first, but the rate of damage tends to decrease during the first stage of corrosion-fatigue, the stage in which the actual stress around the corrosion pits has not reached the ordinary fatigue limit (of an uncorroded specimen). For corrosion-resistant steels, however, damage is at first slow, but tends to accelerate.

The fact that in the authors' tests the tensile properties did not fall off rapidly until the later stages of corrosion-fatigue may be attributed to the fact that the corrosion pits had reduced the section only slightly. If thin sheet metal had been used, however, a different result might have been found. Moreover, if harder steel had been used, the higher stress concentration might have caused a more rapid drop in tensile properties.

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*AUTHORS' REPLY.*

The AUTHORS wrote in reply: We are in general agreement with Mr. McAdam's remarks on the use of tensile tests in the second stage of a two-stage trial. In the work under discussion, the procedure was adopted because severely practical considerations had made it important to gain more knowledge regarding the effect of corrosion-fatigue on the ordinary tensile properties of steel. The dimensions of the specimens were also chosen to conform to service considerations. Mr. McAdam is right in saying that a more slender specimen would have suffered greater damage, although the residual strength will not be determined solely by the reduction in cross-section.

Mr. McAdam's classical two-stage tests on corrosion-fatigue are well known. Actually, in another research which is being carried out in the Cambridge Corrosion Research Section by Mr. Tchorabdji, a two-stage procedure is being followed which employs alternating stress during both stages. The programme differs from that observed by Mr. McAdam in one respect; in the second stage, alternating stresses are continued at the same stress range as in the first stage, but without the application of corrosive solution. The fatigue life, instead of the fatigue limiting stress, serves as a measure of the damage. The points obtained fall well on curves, and are providing some interesting information regarding the mechanism of corrosion-fatigue.

# NOTE ON SOME UNUSUAL MICROSTRUCTURES OBSERVED IN MILD AND MEDIUM-CARBON STEELS.\*

BY T. H. SCHOFIELD, M.Sc.

(Under the direction of Dr. C. Sykes, F.R.S., Superintendent, Metallurgy Department, National Physical Laboratory, Teddington.)

(Figs. 1 to 12 = Plates I. and II.)

## SUMMARY.

Envelopes sometimes observed surrounding the pearlite areas in mild and medium-carbon steels have been shown to be due to the separation of ferrite from the austenite during cooling from temperatures between the lower and upper critical points. By very slow cooling from this critical temperature range or by heating steels showing such envelopes below the lower critical point diffusion takes place and no envelopes are visible.

## *Introduction.*

OCCASIONALLY certain unusual features are observed in the microstructures of mild and medium-carbon steels; the pearlite areas are sometimes surrounded by envelopes the boundaries of which are usually less well defined than the ferrite grain boundaries (Fig. 1). These envelopes disappear after normalising or after heating for some time at temperatures below the lower critical point (Fig. 2), and can be produced again by heating between the lower and upper critical points followed by air-cooling. It was considered that these envelopes might consist of ferrite which had separated from the austenite on cooling; this conclusion is confirmed by the results of the following experiments.

## *Experimental.*

Experiments were first carried out to find out whether the effect observed was general or peculiar to steels of certain composition or manufacture. Samples of seven steels with carbon contents ranging from 0·13% to 0·42% were taken at random from a large batch of steels produced by different processes. Two of the steels were in plate form, two in tube form and the remaining three in bar form. The samples were normalised at 900–950° C., depending on the carbon contents, and were then cut into small specimens each weighing about 6 g.

\* Received September 18, 1943.

In the normalised condition none of the steels showed envelopes surrounding the pearlite areas. Specimens of each steel were reheated for 5 min. at different temperatures between the lower and upper critical points, and in some instances just above the upper critical point, and air-cooled.

All steels which had been heated within the critical range showed envelopes surrounding the pearlite areas, but not when heated above; for example, after heating two steels (*HKE* and *FLE*), containing respectively 0·16% and 0·42% of carbon, at 780° C., which is above the upper critical point for the steel *FLE* but between the lower and upper critical points for the steel *HKE*, envelopes were visible round the pearlite areas of steel *HKE* but not round the pearlite areas of steel *FLE* (Figs. 3 and 4); envelopes round the pearlite areas of the steel *FLE* appeared, however, after heating at 745° C. (Fig. 5).

The definition of the boundaries of the envelopes appeared to depend on the temperature of heating between the lower and upper critical points, and as this definition was good in the steel *HKE* after heating to 780° C. further experiments were limited to this steel and to this temperature, and the effect of the rates of heating and cooling and the time of heating were investigated.

#### *Effect of Rate of Heating to 780° C.*

Three specimens were heated at 150°, 5° and 0·3° C. per min., respectively, to 780° C., held for 5 min. and air-cooled; air-cooling of these specimens corresponds to about 250° C. per min. from 780° to 680° C. The microstructure of all specimens showed envelopes surrounding the pearlite areas, and in all cases the definition of the boundaries of the envelopes was similar (Figs. 3 and 6).

#### *Effect of Time of Heating at 780° C.*

Specimens were heated for 5 and 15 min. and 3 and 24 hr., respectively, at 780° C. and air-cooled; the rate of heating was about 150° C. per min. and the rate of cooling from 780° to 680° C. was again about 250° C. per min. The pearlite areas in each case were surrounded by envelopes which were similar in extent and the boundaries of the envelopes were similarly defined. The pearlite areas within the envelopes were more broken up after heating for 24 hr. than after heating for 5 min. (Figs. 3 and 7).

#### *Effect of Rate of Cooling from 780° C.*

Three specimens were heated at 150° C. per min. to 780° C., held for 5 min. and quenched in water at temperatures of 15°, 60° and 100° C., respectively. A further four specimens were similarly heat-treated and cooled at approximately 250°, 19°, 1° and 0·3° C. per min., respectively.

Figs. 8 and 9 illustrate the microstructures of specimens quenched



FIG. 1.—OTT (Tube) as received. Etched in a solution of nitric acid in alcohol.  $\times 150$ .



FIG. 2.—OTT (Tube) heated at  $680^{\circ}$  C. for 3 hr., air-cooled. Etched in a solution of nitric acid in alcohol.  $\times 150$ .



FIG. 3.—HKE (Bar) heated at  $780^{\circ}$  C. for 5 min. ( $150^{\circ}$  C. per min.), air-cooled ( $250^{\circ}$  C. per min.). Etched in a solution of nitric acid in alcohol.  $\times 500$ .



FIG. 4.—FLE (Plate) heated at  $780^{\circ}$  C. for 5 min., air-cooled ( $250^{\circ}$  C. per min.). Etched in a solution of nitric acid in alcohol.  $\times 500$ .

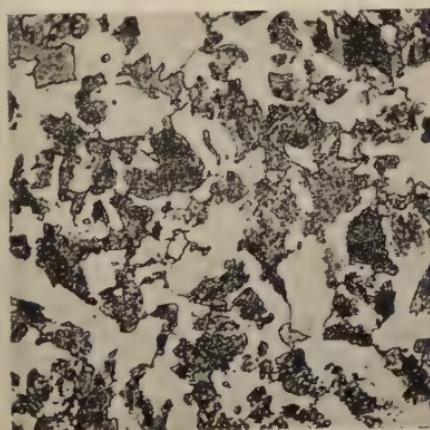


FIG. 5.—FLE (Plate) heated at  $745^{\circ}$  C. for 5 min., air-cooled ( $250^{\circ}$  C. per min.). Etched in a solution of nitric acid in alcohol.  $\times 500$ .

(Micrographs reduced to four-fifths linear in reproduction.)



FIG. 6.—HKE (Bar) heated at  $780^{\circ}$  C. for 5 min. ( $0\text{--}3^{\circ}$  C. per min.), air-cooled ( $250^{\circ}$  C. per min.). Etched in a solution of nitric acid in alcohol.  $\times 500$ .

[Schofield.  
To face p. 120 p.]



FIG. 7.—HKE (Bar) heated at  $780^{\circ}$  C. for 24 hr., air-cooled ( $250^{\circ}$  C. per min.). Etched in a solution of nitric acid in alcohol.  $\times 500$ .

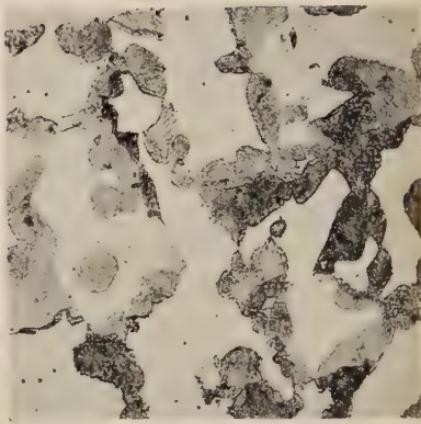


FIG. 8.—HKE (Bar) heated at  $780^{\circ}$  C. for 5 min., quenched in water at  $15^{\circ}$  C. Etched in a solution of nitric acid in alcohol.  $\times 500$ .

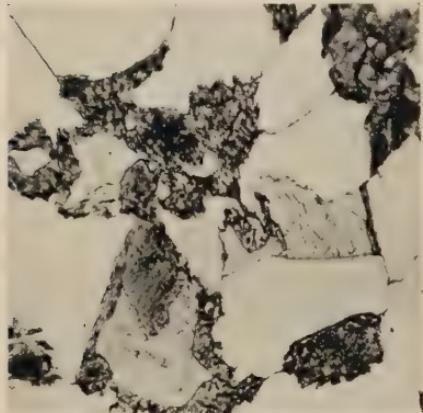


FIG. 9.—HKE (Bar) heated at  $780^{\circ}$  C. for 5 min., quenched in water at  $60^{\circ}$  C. Etched in a solution of nitric acid in alcohol.  $\times 1500$ .



FIG. 10.—HKE (Bar) heated at  $780^{\circ}$  C. for 15 min., air-cooled. Etched in chromic acid electrolytically.  $\times 500$ .



FIG. 11.—HKE (Bar) heated at  $780^{\circ}$  C. for 5 min., furnace-cooled ( $19^{\circ}$  C. per min.). Etched in a solution of nitric acid in alcohol.  $\times 500$ .



FIG. 12.—HKE (Bar) heated at  $780^{\circ}$  C. for 5 min., cooled at  $0\text{--}3^{\circ}$  C. per min. Etched in a solution of nitric acid in alcohol.  $\times 500$ .

(Micrographs reduced to four-fifths linear in reproduction.)

[Schofield.  
To face p. 121 F.

in water at temperatures of 15° and 60° C., respectively. The microstructure of the specimen quenched in water at 15° C. showed areas of martensite in a ferrite matrix, but the areas of martensite were not surrounded by envelopes (Fig. 8). The microstructure of specimens quenched in water at 60° C. (Fig. 9) and 100° C. showed in each case martensite-troostite areas surrounded by envelopes the depth of which was not so great in the specimen water-quenched at 60° C. The areas of martensite in Fig. 8 were similar in shape and size to the fields of pearlite together with the surrounding envelopes (*cf.* Figs. 8 and 3). Fig. 10 shows that the envelopes were darkened by etching electrolytically in chromic acid, which indicates that the envelopes were somewhat different in composition from the ferrite matrix.

The pearlite areas in specimens cooled at 250° and 19° C. per min., respectively, were in each case surrounded by envelopes (Figs. 3 and 11), but in the specimen cooled at 1° C. per min. envelopes were hardly visible.

In the specimen cooled at 0.3° C. per min. no traces of the envelopes remained (Fig. 12).

#### *Summary and Conclusions.*

Envelopes sometimes observed surrounding the pearlite areas in mild and medium-carbon steels result from heating to temperatures between the lower and upper critical points. Such envelopes have been produced in steels of different composition and manufacture and consist of ferrite which has separated at the boundaries of the austenite grains. The extent and definition of the boundaries of the envelopes depend on the temperature of heating and on the rate of cooling. By slowly cooling from temperatures between the lower and upper critical points or by heating steels showing such envelopes for some time below the lower critical point the ferrite which had separated from the austenite diffuses into the surrounding ferrite matrix and the envelopes disappear.

The work described above was carried out as part of the research programme of the National Physical Laboratory, and this paper is published by permission of the Director of the Laboratory.

#### *CORRESPONDENCE.*

Mr. GEO. F. COMSTOCK (The Titanium Alloy Manufacturing Company, Niagara Falls, N.Y., U.S.A.) wrote: The unusual microstructures described so effectively by Mr. Schofield in his note reminded me of structures noticed about twenty-five years ago in some rephosphorised tinplate that was then being studied rather

extensively in our laboratory. These were described by the writer in some "Notes on the Microstructure of Annealed Soft Steel, with Special Reference to Phosphorus in Tin Plate."<sup>1</sup> The conclusion was reached, based on a previous explanation by Whiteley,<sup>2</sup> that the markings which the author calls "envelopes" in the ferrite were due to a lower phosphorus content at that location than in the rest of the ferrite, giving rise to a difference in hardness and etching characteristics. This was checked by etching with Stead's cupric chloride reagent, with about the same results as the author shows for his chromic acid etch. The cause appeared to be that the austenite formed on heating beyond the lower critical point dissolved a portion of the ferrite and caused the phosphorus in it to diffuse into the remaining ferrite because of the carbon in the austenite; and when the austenite decomposed again, on cooling, into pearlite and ferrite, it left the re-formed ferrite lower in phosphorus than the ferrite that had not been dissolved by the austenite.

It would be of considerable interest if the author would report the phosphorus contents of his samples, and state whether he has any evidence that the markings which he has illustrated so clearly require any different explanation from that offered by Whiteley and the present writer years ago.

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#### AUTHOR'S REPLY.

Mr. SCHOFIELD wrote in reply: I thank Mr. Comstock for his remarks and references to previous work. I had occasionally noticed the unusual microstructures in some tube steels and carried out the experiments to find an explanation of them. I was ignorant of Mr. Whiteley's work until after publication. As the unusual microstructures cannot be produced in pure iron-carbon alloys it appears that they are due to one or other of the elements soluble in ferrite and normally present in steels. I have not attempted to find out which element or elements are concerned, and with the facts available cannot offer an alternative explanation to that given by Mr. Whiteley and Mr. Comstock. The phosphorus contents of the steels on which the experiments were carried out are as follows: *OTT*, 0·030%; *FLE*, 0·031%; *HKE*, 0·028%.

<sup>1</sup> *Forging and Heat Treating*, 1921, vol. 7, Jan., p. 60.

<sup>2</sup> *Journal of The Iron and Steel Institute*, 1920, No. I., p. 359.

# THE STRUCTURE OF MARTENSITE.\*

BY H. LIPSON, M.A., D.Sc., AND AUDREY M. B. PARKER, B.A.  
(CAVENDISH LABORATORY, CAMBRIDGE).

(Figs. 6 to 8 = Plate III.)

## SUMMARY.

Some new experimental evidence concerning the structure of martensite has been obtained. It appears that the iron atoms do not lie in an exactly regular arrangement in the tetragonal lattice, such as at the corners and centres of the unit cells, but have a range of structural parameter along the four-fold axis. The mean value of this parameter for a 1.57% carbon steel is about 0.06, which gives a mean displacement, from the special lattice points mentioned above, of about 0.18 Å.

Spatial considerations show that this displacement is such that the octahedral interstices, which Petch (*Journal of The Iron and Steel Institute*, 1943, No. I, p. 221 p) considers to be the most likely positions for the carbon atoms, are enlarged sufficiently to accommodate a carbon atom. This removes the main objection, pointed out by Hägg, to this theory of the positions of the carbon atoms.

The experimental work was done on small rods so that the X-ray and microscopical examinations and the chemical analysis could all be carried out on the same specimen.

Evidence for the displacement of the iron atoms has been obtained from the values of the intensity ratios of the X-ray line doublets given by the tetragonal structure.

MARTENSITE is the main constituent of carbon steel which has been hardened by rapid quenching from the austenitic region. Interest in its structure is aroused particularly by its exceptional hardness, and the first important evidence was obtained by Fink and Campbell,<sup>(1)</sup> who showed that it had a tetragonal space-lattice. Kurdjumow and Kaminsky,<sup>(2)</sup> Öhman<sup>(3)</sup> and others have verified this, and have shown that the *c* and *a* lattice parameters vary linearly with the carbon content. Also the parameter value given by extrapolation to zero carbon content agrees with that for pure iron (body-centred cubic). These facts are in accordance with earlier theories that martensite can be considered as ferrite supersaturated with carbon.

This view is now generally held, and receives support from experimental investigations such as those made by Nishiyama on chromium, nickel and manganese steels.<sup>(4)</sup> He finds that the axial ratio *c/a* depends only on the carbon content, and, moreover, that the tetragonal phase occurs only when carbon is present. The only opposition to this view comes from von Vegenack,<sup>(5)</sup> who maintains, on microscopical evidence, that martensite contains no more carbon than does  $\alpha$ -iron. But his experimental results have

<sup>1</sup> Received August 17, 1943.

not been confirmed by later workers,\* notably Hägg and Öhman,<sup>(6)</sup> and, moreover, his view would not easily account for the tetragonal nature of the space-lattice or its variation with carbon content.

In agreement with the general view, the authors have made the following assumptions :

(a) That carbon is present in martensite.

(b) That the percentage of carbon in the martensite as quenched is the same as that in the austenite from which the martensite has been formed, and that any retained austenite also has this same carbon content. The quenching rate must, of course, be high enough to suppress the formation of fine pearlite, or "nodular troostite."

The next step in the determination of the structure of martensite is the location of the atoms in the unit cell. In this case the task is doubly difficult : First, the structure does not give sharp X-ray diffraction spectra, and cannot be made to do so by annealing, since it is unstable; and, secondly, the carbon atoms are so light that they make only a very small contribution to the intensities of these spectra. This small contribution has been detected on sharp X-ray photographs of austenite,<sup>(7)</sup> but this certainly would not be possible in the case of the indifferent photographs that martensite gives. All the evidence about the position of the carbon atoms has therefore, of necessity, been indirect, and has given rise to some controversy. It is the main purpose of this paper to present some new experimental evidence, which, though still indirect, does seem to indicate more clearly the positions of the carbon atoms, and to reconcile previously divergent points of view.

#### PREVIOUS WORK ON THE POSITIONS OF CARBON ATOMS.

Density measurements<sup>(8)</sup> show that the carbon atoms do not replace any of the iron atoms in the unit cell, but are present

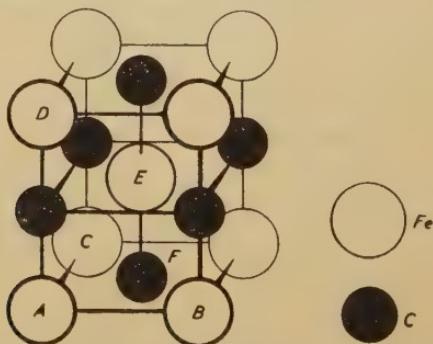


FIG. 1.—The Structure of Martensite as proposed by Petch.<sup>(9)</sup>

\* For a review and discussion of the ideas of von Vegesack, see "Martensite," *Metallurgist*, 1937, vol. 11, p. 9.

interstitially. Petch<sup>(9)</sup> has summarised the evidence for the various possibilities that exist if the iron atoms are at the corners and centres of the unit cells, as they are in  $\alpha$ -iron. He comes to the conclusion that the carbon atoms are in the positions shown in Fig. 1; in such positions they are within octahedra of iron atoms. Petch reaches this conclusion by considering the tetragonal symmetry of the structure, and also the variation in size of the different interstices as the carbon content increases. Yet the chosen interstices are not, as Hägg points out,<sup>(10)</sup> the largest available. Petch therefore concluded that the size of the interstices was not the most important factor in determining the location of the carbon atoms.

### THE SCOPE OF THE PRESENT WORK.

In all the previous work, however, an unnecessary assumption was made, namely, that the iron atoms must be at the corners and centres of the unit cell. This is not necessarily the case, since a displacement along the  $c$ , or four-fold, axis is still consistent with tetragonal symmetry. The co-ordinates of such displaced atoms in any one unit cell may be expressed as  $(0,0,Z_1)$  and  $(\frac{1}{2},\frac{1}{2},\frac{1}{2} + Z_2)$ .

Nevertheless, there is one fact that appears to oppose such a theory of displaced atoms: The only spectra observed are those with  $h + k + l$  even. This would indicate that  $Z_1$  is equal to  $Z_2$ , which is equivalent to putting the atoms again at the corners and centres of the cells, since the origin may be taken at  $(0,0,Z_1)$ . It is possible, however, that a structure such as that of martensite is not built upon normal space-group principles and that atoms are not in similar positions in each unit cell. We may then assume that the atoms are displaced from the corners and centres by different amounts in either direction along the four-fold axes in different parts of the same crystal. If the mean displacement were zero, then the spectra with  $h + k + l$  odd would be absent, as observed.

The intensities of the spectra would be affected, however, and it is these that give a basis for the possible detection of the displacements of the atoms. From the details given in the Appendix it will be seen that the intensities with larger  $l$  index should be relatively weaker than those with smaller  $l$  index.

X-ray powder photographs of martensite were examined visually to see if it would be possible to detect such changes in intensity; it was found that the changes did in fact exist and that even with the poor photographs that martensite gives it should be possible to measure them. A typical photograph is shown in Fig. 6.

The three lowest-order lines on a powder photograph of body-centred cubic iron are line 2, indices 110, line 4, indices 200 and line 6, indices 211, the numbers of the lines being the sums of the squares of the indices. As martensite is tetragonal, with the  $c$  axis greater than the  $a$  axis, the  $l$  indices are not interchangeable

with the others, so that 110, for instance, has a different angle of reflection from 101. Thus, instead of the single line 2 that ferrite gives, there are two lines, one being 110 and the other 101 and 011 which overlap. Since the number,  $p$ , of co-operating planes is in the ratio of 1 : 2, the second line should, in the absence of any displacements of the atoms, be twice as strong as the first. The difference in Bragg angle is small enough for the other factors affecting intensity to be neglected. For the same reason the intensity ratio of lines 002 and 200 + 020, and also of lines 112 and 211 + 121 should be 1 : 2. For convenience these three groups of lines due to the tetragonal phase are described as  $M_2$ ,  $M_4$  and  $M_6$ ; similarly, the austenite lines are described as  $A_3$ ,  $A_4$ , &c.

If there is a variation of intensity with the value of  $l$ , then the intensity ratio for  $M_2$  will be less than 2 : 1, while the ratios for  $M_4$  and  $M_6$  will be greater than 2 : 1. The intensity ratios were therefore measured in order to see if these values gave reasonable quantitative agreement with those to be expected if the iron atoms were displaced, and to obtain an approximate value for this displacement.

#### EXPERIMENTAL DETAILS.

Preliminary experiments were carried out on quenched iron-carbon powders, but it was decided to proceed with further experiments on small rods cut from the lump. Despite the possibility of preferred orientation in the rod, this method has several advantages :

- (1) The risk of introducing impurities into the specimen is reduced.
- (2) Micro-analysis can be carried out on the actual specimen used for the X-ray photographs.
- (3) The specimen can be examined microscopically for inhomogeneity and for the presence of extra phases. This is particularly important.
- (4) Powders do not always give the same results as lumps of the same alloy. Petch<sup>(7)</sup> has suggested that this discrepancy is due to the increased ratio of surface to volume. Since martensite is believed to exist in a state of high internal strain, this may affect the results particularly in this case.

The alloy used was made from Hilger's electrolytic iron (No. F693) and Hilger's graphite (No. F623). These were melted together in a magnesia crucible in a hydrogen atmosphere by means of an induction furnace, and allowed to cool *in vacuo*. Microscopic examination showed that the alloy was homogeneous, so no further homogenising treatment was given.

Rods of about 0.5 mm. square cross-section and 1-2 cm. long were cut from the centre of the lump; they were sealed in evacuated silica tubes and quenched in 10% brine after holding for 15 min.

at 1000° C. It is realised that the silica tube reduces the quenching rate, but it was found possible with the above treatment to avoid the formation of fine pearlite, except in the case of one rod, marked 2a. This observation was made microscopically, the specimen being held in a small steel clamp during the preparation for examination.

X-ray photographs of the martensite rods were taken in a 9-cm. Debye-Scherrer powder camera, the rod being rotated throughout the exposure. The amount of retained austenite was reduced by immersion in liquid air. Fe  $K\alpha$  radiation was mainly used, but in order to examine a particular point that arose, both Co  $K\alpha$  and

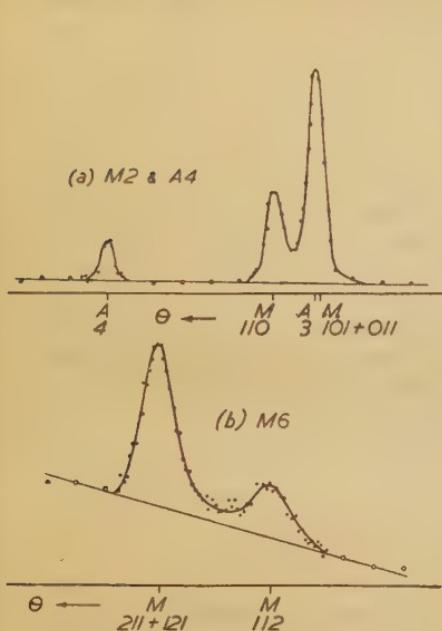


FIG. 2.—Photometer Curves for (a)  $M_2$  and  $A_4$ , and (b)  $M_6$ .

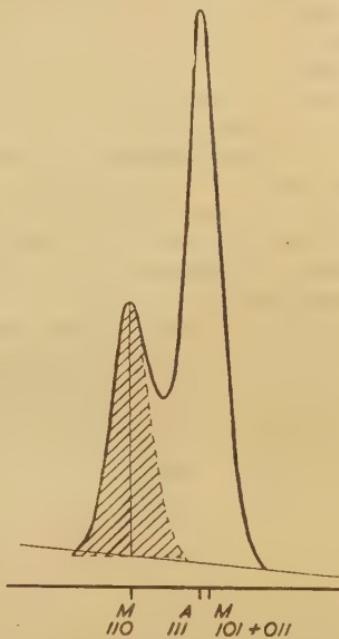


FIG. 3.—Method of Analysis of  $M_2$ .

$Cr K\alpha$  were also used. Crystal-reflected monochromatic radiation, from a penta-erythritol crystal, was also employed in some cases in order to reduce the background.

The photographs were photometered by means of a micro-photometer of the Dobson type.<sup>(7)</sup> Readings were taken at intervals of 0.1 mm. along the film, and correction for non-linearity in the blackening-intensity curve was made from calibration strips put on the film by means of a rotating stepped sector. This correction was necessary in only a few cases for  $M_2$ . The intensity readings were plotted against distance along the film, and the background was found by interpolating between the readings of the background on either side of each pair of lines.

Some typical results are given in Fig. 2; these show (a) the

components of  $M2$  and the smaller peak due to  $A4$ , and (b) the components of  $M6$ . The figures illustrate two important points: First, the background is not reached between the two components of the martensite lines, and this is also the case for lines  $M4$ ; secondly, the amount of retained austenite is not negligible and must be taken into account in estimating the intensity ratio of  $M2$ , since another austenite line,  $A3$ , lies in the  $M2$  group in the position shown. The following methods were used in taking these facts into account. The  $A3$  line lies nearest to  $011 + 101$  and has no effect on the outer half of the  $110$  component. The total area of the latter can thus be taken as that of a line symmetrical about the peak value, that is, the area shown shaded in Fig. 3. The intensity of the other component was found from the total area by subtraction of the area of the  $110$  component and also of the area of  $A3$  as calculated from  $A4$ .

The other doublets,  $M4$  and  $M6$ , have no overlapping austenite lines, and ordinary methods of resolving intensities can be used. For this reason  $M4$  and  $M6$  should give more reliable results than  $M2$ .  $M4$ , however, is relatively weak, and  $M6$  gives better results, although its angular separation is less. Unfortunately none of the indices  $211$  is zero, so that the information given by  $M6$  is not so easily interpreted. It will thus be appreciated that the method is not capable of any very great degree of accuracy. Random errors of the order of 20% are quite possible, and in the case of  $M2$  systematic errors may also arise both from the correction for  $A3$  and from the method of separating the components. Systematic errors arising from the method of separation will be smaller in the case of  $M4$  and  $M6$ , owing to the greater separation of the components.

#### RESULTS.

The main work was done on two rods, designated  $2a$  and  $2x$ , cut from the same ingot. A carbon estimation by direct combustion in a current of oxygen at  $1200^\circ\text{ C}$ . in a micro-furnace, made on rod  $2x$  in the Metallurgy Department of the National Physical Laboratory, gave the carbon content as 1.57%. For reasons that will be described later, it was considered that the results from the various lines were not self-consistent, and it was decided to see if the inconsistency could be ascribed to inhomogeneity of the specimen.

Fig. 4 shows how such inhomogeneity could affect the relative intensity of the X-ray spectra. Two rays are drawn with the same distance of traversal of a circular specimen; the ray with the higher Bragg angle penetrates more deeply.

Two methods for detecting such effects were tried, (a) the etching-away of the outer surface to expose the interior, and (b) the use of different radiations with correspondingly different absorption coefficients.

In Table I. the results of the etching experiments are presented. *M*2 and *M*6 do show a systematic variation, although it is hardly greater than the probable error. The results for *M*4 are apparently still less reliable.

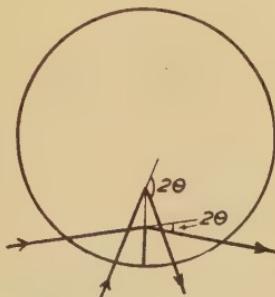


FIG. 4.—The Increase of Penetration with  $\theta$ .

The results for different radiations, given in Table II., are more decisive. *M*2 shows an insignificant increase with decrease of wave-length; *M*4 was not clear enough for photometry except in the photograph with Co *K* radiation; *M*6 shows an increase that is definitely larger than the experimental error.

TABLE I.—*Homogeneity of the Specimen. Examination by Etching-away the Surface.*

Specimen, rod 2a. Radiation, Fe *K*.

Film.	Treatment.	Intensity Ratios.		
		<i>M</i> 2.	<i>M</i> 4.	<i>M</i> 6.
4296	As quenched	...	3.68	3.64
4297	After microscopic examination	...	3.63	3.49
4308		1.58	...	3.44
4312	$3.6 \times 10^{-3}$ cm. removed	1.79	4.44	3.47
4313	$5.0 \times 10^{-3}$ cm. removed	2.01	3.53	3.14
4315	$2.2 \times 10^{-3}$ cm. removed	2.06	...	3.19
		1.93	...	3.01

In order to see if there were any variation of carbon content the lattice parameters were measured after the various etchings. The method used was as follows: A value for the axial ratio was obtained from *M*4 and this was used in calculating *c* and *a* from each of the lines *M*6. The value of *a* can also be obtained from 220, and the true value was found by extrapolating linearly against  $\sin^2\theta$  to  $\sin^2\theta = 1$ .<sup>(12)</sup> The value of *c* was obtained by parallel extrapolation through the value from *M*6. The accuracy to be expected from such methods is much less than is usually attained

TABLE II.—*Homogeneity of the Specimen. Examination by using Different Radiations.*

Film.	Radiation.	Intensity Ratios.					
		M2.		M4.		M6.	
		Readings.	Mean.	Readings.	Mean.	Readings.	Mean.
4687	Cr K $\alpha$ . $\lambda = 2.28632 \text{ kX.}^*$	1.27 1.49 1.26	1.38	...	...	4.37 4.76	4.57
4650				...	...	...	
4659	Fe K $\alpha$ . $\lambda = 1.93338 \text{ kX.}^*$	1.53 1.67 1.25 ...	1.43	...	...	...	4.15
4664				...	...	4.14 4.16	
4591		1.92		...	...	...	
4584	Co K $\alpha$ . $\lambda = 1.78659 \text{ kX.}^*$	1.46 ...	1.53	3.27 3.54	3.40	2.68 3.03 3.09 3.24	3.01
4761		1.40 1.32		...	...	...	

\* Since it is now known that the unit of X-ray wave-length—the X-unit—differs from  $10^{-11}$  cm. by 0.2%, the values of distances deduced in previous X-ray work, if expressed in Ångstrom units ( $10^{-8}$  cm.), have been wrong by this amount. It has been thought advisable, however, to retain the X-scale for the time being and so the term kX. (kilo-X-unit) (11) is used in this paper. It is admitted that, for most of the quantities recorded, the difference between 1 Å. and 1 kX. is negligible, but for the sake of consistency it was thought advisable to use only the one unit.

in spacing measurements, but even so the deductions are fairly precise. The results in Table III. show no significant variation, and if it is assumed that the axial ratio is constant within an

TABLE III.—*Determination of Uniformity of Carbon Distribution in the Specimens.*

Specimen.	Film.	c Parameter. kX.*	a Parameter. kX.*	Ratio c/a.
Rod 2x.	4761	3.031	2.842	1.066
Rod 2a	4297	3.036	2.853	1.064
	4312	3.040	2.845	1.069
	4313	3.039	2.850	1.066
	4315	3.040	2.847	1.067
Mean	...	3.037	2.847	1.066

\* See footnote to Table II.

accuracy of  $\pm 0.003$ , then the carbon content must be constant to within  $\pm 0.08\%$ . It therefore seems safe to conclude that there is no appreciable variation of carbon content within the specimen 2a.

#### INTERPRETATION OF THE RESULTS.

Despite the inaccurate nature of the results it is possible to reach some quantitative conclusions. Nevertheless, it is first

necessary to consider whether there is any other way of interpreting the observed results.

It is obvious that the presence of retained austenite could not introduce any systematic error. The presence of ferrite, however, would do so; the  $a$  axis of martensite is not greatly different from that of ferrite ( $2\cdot8604$  kX.\*), so that any ferrite present would give lines that would partially overlap with those lines of the martensite doublets which have the lowest  $l$  index. The presence of ferrite would therefore have the same general effect as a displacement of the iron atoms, but it would not account for the actual intensity ratios which are observed. For instance, roughly 25% of ferrite combined with a martensite in which the atoms lay on the corners and edges of the tetragonal unit cell would account for the intensity ratios of  $M_4$  and  $M_6$ , but would make that of  $M_2$  equal to unity. However, it is still of importance to check, by microscopic examination, that no appreciable quantity of ferrite is present, a fact that has been referred to before when dealing with the advantages of rod specimens over powders. A very small amount of ferrite was present in the fine pearlite in rod  $2a$  (see Fig. 7) and none at all was detected in rod  $2x$  (see Fig. 8). Thus, it does not appear that the results can be ascribed to the presence of ferrite.

Another possible, but not very likely, way of accounting for the results could be by the occurrence of preferred orientation. However, similar intensity ratios were obtained with powder specimens in which preferred orientation is improbable. These results are not quoted in this paper, because there was no means of checking that the specimens contained no ferrite.

A third possibility is an anisotropy of temperature motion. If the thermal vibrations of the atoms were much larger in the  $c$  direction than in the  $a$  and  $b$  directions the formula for the intensities would be similar to that given for a Gaussian distribution of displacements of the atoms (see Appendix). Brindley<sup>(13)</sup> claims to have found such anisotropy in zinc, but the effect is small; in martensite it would have to be improbably large to explain the observed results.

No other possibility has suggested itself to the authors. They therefore feel justified in assuming that the results support the theory that the iron atoms in martensite are displaced from the corners and centres of the cells.

The discussion that follows will be clarified by reference to Table IV., which gives the values of the intensity ratios that would result from different displacements. The data from  $M_2$  are not as decisive as those from  $M_4$  and  $M_6$ , since the intensity ratio varies much more slowly. An error of 20% in  $M_2$  would correspond to a displacement of  $0\cdot2$  kX.  $M_4$  and  $M_6$  are more definite, and, despite the variation shown in Tables I. and II., the displacements must be in the neighbourhood of  $0\cdot17$ – $0\cdot20$  kX. The structure of martensite can thus be represented by Fig. 5, in which the

\* See footnote to Table II.

TABLE IV.—*Theoretical Values of Intensity Ratios.*

Mean Displace- ment, $kX$ .	Intensity Ratios.		
	$M_2$ .	$M_4$ .	$M_6$ .
0.00	2.00	2.00	2.00
0.02	2.00	2.02	2.01
0.04	1.99	2.06	2.04
0.06	1.98	2.13	2.10
0.08	1.95	2.24	2.18
0.10	1.92	2.39	2.28
0.12	1.88	2.59	2.43
0.14	1.84	2.87	2.63
0.16	1.79	3.22	2.88
0.18	1.74	3.71	3.22
0.20	1.68	4.38	3.68
0.22	1.62	5.3	4.3
0.24	1.54	6.7	5.2
0.26	1.47	8.9	6.6
0.28	1.39	12.6	8.8
0.30	1.32	19.3	12.8

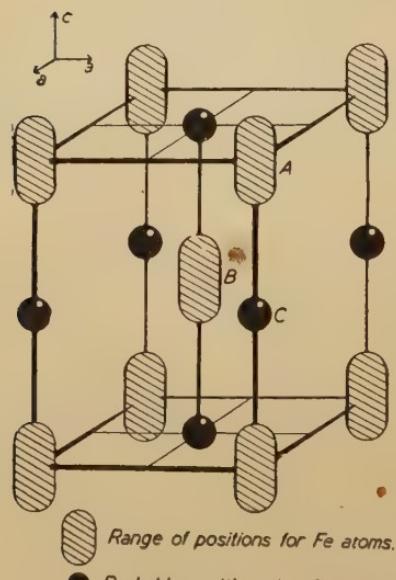


FIG. 5.—Proposed Structure of Martensite.

$c/a$  ratio is considerably exaggerated. The iron atoms are shown as elongated along the  $c$  axis, the range of possible positions being included within  $\pm 0.20$  kX. In actual fact it is to be expected that the iron atoms will occupy a range of values considerably greater than this, since 0.20 kX. is an average value. The black spots represent the possible positions for the carbon atoms as suggested by Petch,<sup>(9)</sup> but only  $\frac{1}{2}$  of them are occupied for a carbon content of 1.7%.

These positions are also consistent with the displacement of the iron atoms if it is assumed that the Fe-C interatomic distances tend to the values that they have in cementite.<sup>(14)</sup> These values range from 1.85 to 2.15 kX., with a mean value of 2.03 kX. The interatomic distance in the (001) plane of martensite is 2.01 kX., which is in agreement with these values. But if the iron atoms are in the (000) and  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  positions, the interatomic distance in the [001] direction is 1.51 kX., which is rather small. If it is assumed that an iron atom adjacent to a carbon atom in the [001] direction can attain a maximum displacement of as much as three times the mean value, then the interatomic distance in this direction becomes roughly 2 kX. Thus, the displacement provides evidence, additional to the tetragonal symmetry itself, in favour of the indicated positions of the carbon atoms. Also, the structure now satisfies Hägg's condition that the carbon atoms should be in the largest interstices available.

There is probably also some random displacement, with mean value zero, in the (001) plane. Such displacements would not be due directly to the carbon atoms, since there is no overcrowding in the (001) plane, as the interatomic distances in the previous paragraph show. They are more likely to arise as components of the displacements caused by those of neighbouring iron atoms along the  $c$  axis. Such components should, however, be small in comparison with components along the  $c$  axis.

Displacements in the (001) plane would have an effect on the intensities opposite to that caused by a displacement in the [001] direction. If there is any such displacement, it cannot be detected by the methods used in this investigation. It would mean that the value found for the mean of the displacements along the  $c$  axis is less than the true value.

The mean value of the displacement along the  $c$  axis may be expected to vary with the carbon content, for the smaller the number of carbon atoms the smaller is the number of iron atoms that will be displaced by the maximum amount. If the systematic tendencies in Tables I. and II. are accepted as real, then the displacement is also greater at the surface than in the interior of the specimens used. It is difficult to account for this; decarburisation at the surface, for instance, would produce the opposite effect. It is more probable that it is due in some way to the more rapid quenching at the surface, and further examination of this point may provide interesting information.

## HARDNESS OF MARTENSITE.

The hardness of martensite is probably bound up with its tetragonal nature. Lipson, Shoenberg and Stupart<sup>(15)</sup> have shown that the alloy FePt, which also has a tetragonal unit cell with an axial ratio of almost unity, has a particularly high magnetic hardness. This was attributed to the displacements of the atoms caused by their attempts to fit the tetragonal unit cells into a cubic lattice. Martensite, which has an axial ratio even further from unity, might be expected to have a similarly distorted lattice, although in the absence of an exact definition of hardness the authors do not wish to stress this possible correlation with structure.

## ACKNOWLEDGMENTS.

The authors wish to thank Professor Sir Lawrence Bragg, F.R.S., and Dr. A. J. Bradley, F.R.S., for their interest and encouragement. The work has been done for the Structure of Alloys Research Panel of the British Iron and Steel Federation.

APPENDIX.—*Determination of the Structure Amplitude.*

The intensity of a line on a powder photograph is given by :

$$I = F^2_{(hkl)} \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot p \cdot A \cdot e^{-B\left(\frac{\sin \theta}{A}\right)},$$

where  $F$  is the structure amplitude,  $\theta$  the Bragg angle,  $p$  the number of co-operating planes,  $A$  the absorption coefficient, and the last term the temperature factor. The structure amplitude is the term affected by the displacement, since its value is given by :

$$F_{(hkl)} = f_{Fe}[e^{2\pi i l z_1} + e^{2\pi i l (\frac{h+k+l}{2} + l z_2)}],$$

where  $f_{Fe}$  is the atomic structure factor for iron.

If  $z_1$  is assumed to be equal to  $z_2$ , and the displacements of all iron atoms are supposed equal to a mean value  $z$ , the sign of which is equally likely to be positive or negative, then the structure amplitude is given by :

$$F_{(hkl)} = f_{Fe}(e^{2\pi i l z} + e^{-2\pi i l z} + e^{+2\pi i \left[\frac{h+k+l}{2} + l z\right]} + e^{+2\pi i \left[\frac{h+k+l}{2} - l z\right]}).$$

$$\therefore F^2 = 4f^2 \cos^2 2\pi l z.$$

It might give a closer approximation to the truth to assume a Gaussian distribution of iron atoms about the special positions, in which case the structure amplitude becomes :

$$F^2 = 4f^2 \int_0^\infty \cos^2 2\pi l z \frac{a}{\sqrt{\pi}} e^{-az^2} dz.$$

$$\approx 2f^2 e^{-\frac{\pi^2 l^2}{a^2}}.$$



FIG. 7.—Rod 2a; fine pearlite at grain boundaries.  
Lightly etched with 2% nital solution.  $\times 1000$ .

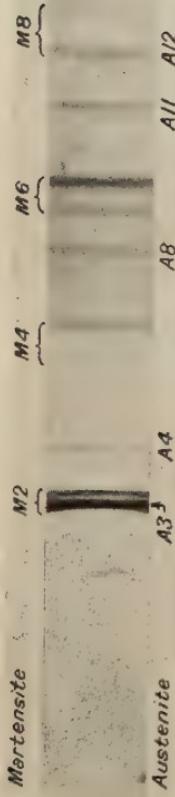


FIG. 6.—X-Ray Photograph of Martensite with Retained Austenite. Co  $K\alpha$  radiation Fe filter.



FIG. 8.—Rod 2x. Severely etched with 2% nital solution.  $\times 750$ .

[Lipson and Parker.  
[To face p. 134 p.]



FIG. C.—Micro-Cracks in a 1.1% Carbon Steel Quenched from above the  $A_{cm}$  point. Sample first etched to reveal micro-cracks clearly, repolished and re-etched to show martensite structure. Etched in 1% nital.  $\times 800$ .



FIG. D.—Plain 0.26% Carbon Steel suddenly heated above  $A_{c1}$  and air-cooled. Pearlite grains transformed (sometimes only partially) into martensite grains embedded in ferrite. Etched in 1% nital.  $\times 250$ .

[*Wrazej on Lipson and Parker.*  
[To face p. 135 p.]

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## CORRESPONDENCE.

(Figs. C and D = Plate IIIA.)

Dr. Ing. W. J. WRAŻEJ (Technical Research Institute, General Staff, Polish Army) wrote : Sir Harold Carpenter and J. M. Robertson<sup>1</sup> said that the development of the tetragonal lattice was due simply to the modification of the iron lattice by the inclusion of carbon. This tetragonality, according to the present authors, can be expressed by the mean value  $c/a = 1.066$ , where  $a = 2.847 \text{ kX}$ . and  $c = 3.037 \text{ kX}$ . The displacement of an iron atom can be taken as  $\pm 0.20 \text{ kX}$ . The mean value of the displacement of an iron atom in the  $\alpha$ -iron lattice, however, can, as the authors say, alter with the carbon content.

N. J. Petch<sup>2</sup> stated that in martensite one-twelfth of the available interstices seemed to be filled with carbon atoms.

Regarding the  $\alpha$ -iron lattice (body-centred cubic) as built up of two sets of interpenetrating simple cubic lattices, the carbon atoms situated at, for instance, the  $(\frac{1}{2}\frac{1}{2}1)$  positions in the first set of such lattices must be regarded as being situated at the edges of the second set of simple interpenetrating cubes, causing the same displacement of adjacent iron atoms.

<sup>1</sup> "Metals," vol. II., p. 890. Oxford, 1939 : University Press.<sup>2</sup> *Journal of The Iron and Steel Institute*, 1943, No. I., p. 221 p.

Attention must be directed to certain features after quenching a hypereutectoid steel. In order to bring into solution the whole of the cementite in such a steel it must, as is well known, be heated to higher temperatures ( $A_{cm}$ ) than those necessary for a eutectoid steel. The authors heated a 1.57% carbon steel to 1000° C., and as a result a not negligible amount of retained austenite was present besides martensite; with a hypereutectoid steel, using a lower temperature than  $A_{cm}$ , cementite residues are to be expected.

When austenite is present even only in traces one can never be certain how much of the carbon remains in the austenite and how much in the martensite. When free cementite exists in a steel quenched from the  $Ac_1$  temperature, the martensite formed will contain only the amount of carbon associated with the pearlite.

The above remarks rather suggest that in plain carbon steels a perfect martensite should be expected in a steel of eutectoid composition.

Considering the number of carbon atoms in a martensite containing 1.7% or 0.8–0.9% of carbon, let us calculate the number of their positions. With six available places for carbon, *i.e.*, two atoms of carbon in a two-atomic unit cell of iron, according to Petch and to the present authors, a simple calculation shows that there would be about 82.3% of iron and 17.7% of carbon if all the places were filled. When  $a = 2.847 \text{ kX}$  and  $c = 3.037 \text{ kX}$ , as the authors say, there will be about  $40.63 \times 10^{21}$  unit cells in 1 c.c. of iron or  $81.26 \times 10^{21}$  atoms of iron. If 55.84 be taken as the atomic weight of iron and 12.01 as that of carbon, this gives the amount of iron and carbon stated above.

Of greatest interest to industry are, as is well known, the steels with 0.8–0.9% of carbon (*i.e.*, eutectoid steels). In these only one-twenty-fourth to one-twentieth of the carbon atoms can be placed in the positions available in the unit cell shown by Petch and by the authors. This represents, say, one carbon atom for twelve lattice units.<sup>1</sup> Taking the case of a quenched eutectoid steel, if that one carbon atom is inserted in the lattice of  $\alpha$ -iron (Fig. A) it can be seen that the set of, say, twelve  $\alpha$ -iron lattice units can, in fact, be distorted (*see* Fig. B) by the single carbon atom, which is in accordance with the views of Petch and the authors.

Fig. B shows that this single carbon atom is surrounded by an octahedron of iron atoms; it is most centrally situated among the twelve unit cells. According to Petch, in the octahedral interstices of a carbon-free steel, four of the iron atoms are at a distance which leaves 0.77 Å. excess; the other two, however, leave only 0.18 Å., so that none of the interstices is large enough to accommodate a carbon atom of radius 0.77 Å. without displacement of the neighbouring iron atoms.

The very symmetrical position of a single carbon atom in the

<sup>1</sup> In that case the eutectoid composition, *i.e.*, one carbon atom to 24 iron atoms, would correspond to about 0.885% of carbon in the steel.

martensite in a eutectoid steel provides an explanation of the fact that the excess of carbon in a hypereutectoid steel tends to precipitate easily in the form of free cementite. This is not the case, however, when this excess of carbon can be retained in austenite residues, which can easily accommodate more carbon atoms (even 0.32 atom per unit cell in saturated solid solutions) than martensite.

The diffusion of the lines  $M_4$ ,  $M_6$  and  $M_8$  in the authors' Fig. 6 gives evidence that the lattice seems not to be perfectly tetragonal but tetragonally distorted. This points the way to the explanation

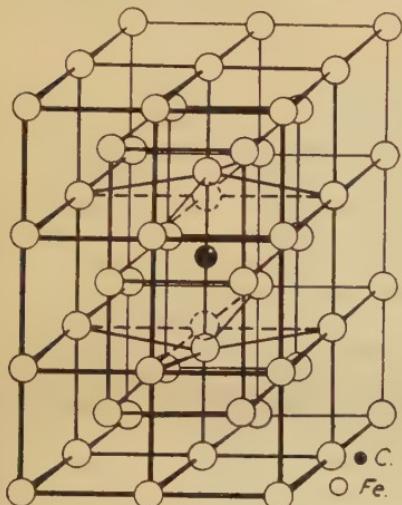


FIG. A.—Atomic Arrangement in Martensite in Eutectoid Steel. One carbon atom distorts twelve  $\alpha$ -iron unit cells. For clarity only two displaced iron atoms shown.

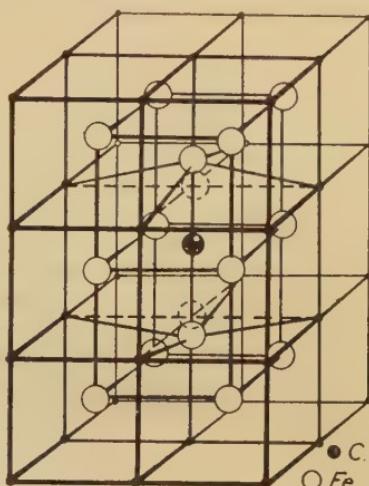


FIG. B.—Simplified Drawing of Fig. A (iron atoms at corners indicated by dots), showing displacement of iron atoms and that the carbon atom on one edge of the first set of simple cubes must be regarded as situated in the face of the second set of simple cubes.

why such a distorted martensite lattice (Fig. B), although only slightly tetragonal ( $c/a = 1.066$ ), does not possess any easy gliding planes, *e.g.*, (110), (112), (123) with glide direction [111], as were given for cubic metals by E. N. da C. Andrade and others.<sup>1</sup>

The gliding planes as well as the glide direction mentioned above would be affected by the distortion of the martensite lattice. Micro-cracks have hardly ever been observed to pass through martensite grains (Fig. C), as the latter are strongly resistant to cracking. In this way it can be seen that not the tetragonal character itself but rather the distortion of the lattice seems to be responsible for the hardness of martensite, owing to the lack of easy gliding possi-

<sup>1</sup> *Proceedings of the Physical Society*, 1940, vol. 52, Part 1, p. 3.

bilities in it. The hardness test, consisting of the pressing of a diamond or ball into the material, can be considered as a purely plastic deformation process based on the development of gliding planes. In the case of martensite this is not easy, which accounts for its hardness.

There are many features in quenched steels which support the opinion that the martensite structure can form easily in a eutectoid steel; such martensite must be regarded as "ideal." The presence of less or more carbon in the steel will not only require higher temperatures to bring the carbon present into uniform solid solution, but also during quenching it will cause the precipitation of ferrite or cementite.

The  $\alpha$ - $\gamma$  change takes place most easily in a eutectoid steel. Even on sudden heating pearlite transforms easily into austenite. Fig. D shows an example of a plain 0·26% carbon steel that had been suddenly heated and then air-cooled; the short time at a temperature slightly above the  $Ac_1$  point was sufficient to transform the pearlite into austenite. Some of the pearlite grains are only partially transformed, because either the correct transformation temperature ( $Ac_1$ ) had not penetrated very deeply into the material or the cooling rate was too slow for that region. The first explanation is the more likely. This shows that in the martensite in eutectoid steel the carbon can be accommodated particularly easily, owing to the symmetrical distribution of the carbon atoms in the  $\alpha$ -iron lattice; this martensite must be regarded as one of the most "stable" forms. The suggestion made above that one carbon atom placed among twelve  $\alpha$ -iron unit cells is the most probable form in the martensite in eutectoid steel seems to approach most closely to actuality.

The writer wishes to thank Dr. C. H. Desch, F.R.S., and Professor C. W. Dannatt for their interest in and valuable criticism of the foregoing contribution.

Dr. N. J. PETCH (Farnborough, Hants.) wrote : Considering the nature of the X-ray diffraction lines given by martensite and the disappointing results which arise in the photometry of lines unless they are sharp and fairly strong, the achievement of the authors in obtaining evidence of the nature of the martensite structure makes this paper very interesting. There are, however, two points upon which I would like to comment.

The authors state that in all previous work "an unnecessary assumption was made, namely, that the iron atoms must be at the corners and centres of the unit cells." I do not think that this is quite the case. Other workers may not have dealt so fully with the fact that in a martensite crystal the length of the  $c$  axis will not be the same in all the unit cells, this being the point which the authors demonstrate by their intensity measurements, but I

would hesitate to conclude that the above-mentioned assumption was in fact made. It has long been recognised, e.g., by Seljakow, Kurdjumoff and Goodtzow,<sup>1</sup> that not all of the possible carbon positions in the martensite structure are filled; indeed, with most martensites there will, at any instant, be no carbon atoms at all in some of the unit cells. Thus the length of the *c* axis in such cells will differ from the value in those containing carbon, and the cell size indicated by the X-ray measurement will be some average value. I feel that the appreciation of the point made by the authors follows directly from the appreciation that not all the carbon positions are filled, and must have been recognised by those who have given thought to the martensite structure. In metallic alloys rather similar variation between the unit cells must occur, although it is not often emphasised. In my own paper,<sup>2</sup> on the positions of the carbon atoms in martensite, having pointed out that with the dimensions corresponding to 0% of carbon none of the interstices is large enough to accommodate a carbon atom of radius 0.77 Å. without requiring displacement of the neighbouring iron atoms, I wrote "it is not, however, immediately possible to decide where the carbon atoms must be located in order to give the observed dimensions, because with the practical carbon contents only a fraction of the available interstices of any kind can be filled." I would suggest that this indicates an appreciation of the fact that in martensite the size of an interstice occupied by carbon will be different from that of an unoccupied one and that the size observed by X-rays is some average value—in fact, that not all the unit cells in a crystal have the same dimensions.

The authors also consider that an answer has been found to the objections raised by Hägg to the supposition that the carbon atoms in martensite are in octahedral interstices. I think that this is hardly a fact. If there is no carbon in martensite the structure is, of course, that of  $\alpha$ -iron, and it has already been pointed out that none of the interstices is large enough to accommodate carbon atoms without there being displacement of the iron atoms. The tetrahedral interstices, however, are larger than the octahedral ones. Hägg's point was that the comparison of the rate at which the volume of martensite increases with carbon content with the rate for austenite suggests that the tetrahedral interstices in martensite are utilised, since, being initially the largest in the structure, they will require least displacement of the iron atoms to permit accommodation of carbon atoms. He was thus concerned with the size of the interstices before any carbon was present, so the fact, advanced by the present authors, that the size of an octahedral interstice, once it has been enlarged by the presence of carbon in it, is greater than that of a tetrahedral one which has not been so enlarged, is

<sup>1</sup> Seljakow, Kurdjumoff and Goodtzow, *Zeitschrift für Physik*, 1927, vol. 45, p. 384.

<sup>2</sup> Patch, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 221 P.

hardly relevant. Actually Hägg's conclusion is merely an expression of opinion on what interpretation should be put on certain facts, and, as it happens, this interpretation is wrong. It is possible to understand where the fallacy arises. In austenite<sup>1</sup> the interstices utilised are octahedral, and insertion of a carbon atom will cause primary displacement of the six iron atoms, whereas in martensite the dimensions of the octahedral interstices are such that insertion only produces primary displacement of two iron atoms. In the martensite tetrahedral interstices there will be displacement of four iron atoms. Thus, on account of the difference in the number of iron atoms which suffer displacement, the simple basis on which Hägg reasoned about the volume changes is not permissible.

In my opinion<sup>2</sup> the location of the carbon atoms in selected octahedral interstices in martensite is probably a result of its formation from austenite by slip movement of planes of iron atoms, during which the carbon atoms are retained in the interstices which they originally occupied. Incidentally, since normally in slip a number of neighbouring unit cells behave in a similar manner, giving glide lamellæ, this would supply a reason for the octahedral interstices utilised being such that a number of neighbouring martensite unit cells all have their *c* axes in a common direction, this being a necessary condition for the detection of the tetragonality by X-rays. Without some such explanation, the co-operation between neighbouring unit cells would present a difficulty in the understanding of the martensite structure. The reason why the carbon atoms remain in the octahedral interstices, although they could readily move aside into the tetrahedral ones, remains unexplained. Considering the atoms as hard spheres may not, however, give the correct picture.<sup>2</sup> Another possibility is that, even considering the atom as a sphere, the greater initial size for carbon accommodation of the tetrahedral interstices may be illusory, since, as already mentioned, carbon insertions would involve primary displacement of four iron atoms, whereas in the octahedral interstices, although the displacement required is greater, it is confined to two atoms.

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#### AUTHORS' REPLY.

The AUTHORS wrote in reply : Dr. Wrażej's interpretation of our proposed structure of martensite differs somewhat from our own. Our Fig. 5 was intended to indicate that only two iron atoms are directly displaced by the insertion of one carbon atom, although others will be indirectly displaced. It is true, of course, that twelve unit cells will be affected, but this seems to put too much emphasis on the concept "unit cell," which, after all, is merely

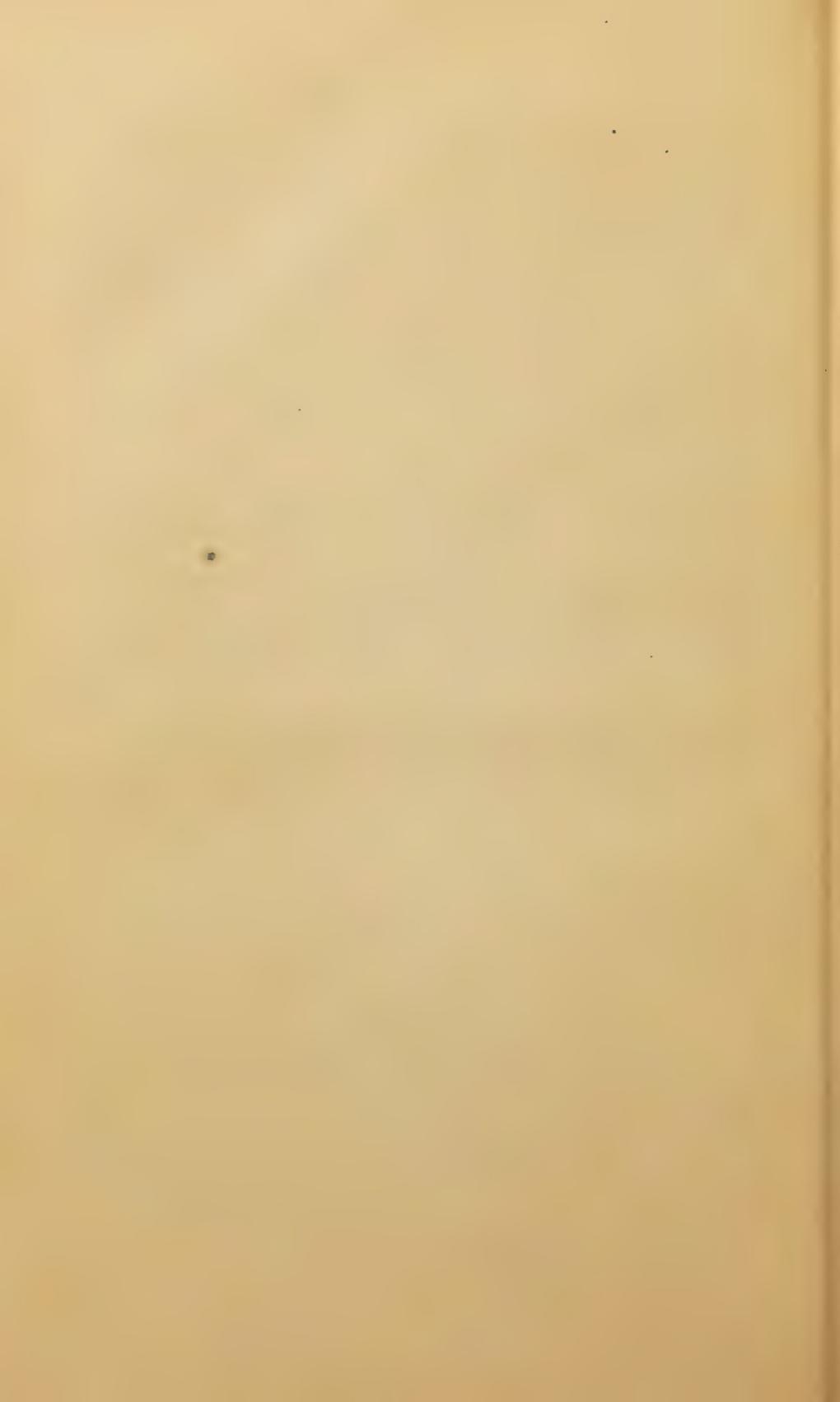
<sup>1</sup> Petch, *Journal of The Iron and Steel Institute*, 1942, No. I., p. 111 p.

<sup>2</sup> Petch, *Journal of The Iron and Steel Institute*, 1943, No. I., p. 221 p.

introduced in order to simplify crystallographic calculations. Certainly this number twelve has no obvious relation to the ratio of the number of available sites to the *maximum* number filled by carbon atoms.

We are in general agreement with the views stated by Dr. Petch, but we thought it worth while to state explicitly what had only been implied before—that the iron atoms are displaced from the corners and centres of the unit cells; Dr. Petch's own paper, for instance, includes a figure (our Fig. 1) which shows the iron atoms at these positions. He justifies this by stating that he did not intend all the unit cells to be of the same size; this would lead to the same structure as ours, but would be a rather difficult concept to treat theoretically: our method of considering a perfect lattice with the atoms displaced from the lattice points has proved much more fruitful.

We still feel that our structure reconciles the two theories discussed by Dr. Petch, and in fact we find it difficult to express this more clearly than Dr. Petch himself has done. One does not imagine a carbon atom searching for an interstice large enough into which to insert itself; according to present-day views of atomic migration it is more likely to try various positions and to settle in those in which it produces the smallest increase of free energy. From this point of view there is no need to consider at all the interstices in carbon-free iron.



# THE INTERPRETATION OF THE CRYSTAL STRUCTURE OF CEMENTITE.\*

BY N. J. PETCH, B.Sc., B.MET. (FARNBOROUGH, HAMPSHIRE).

## SUMMARY.

Previous work on the structure of cementite with which the author was associated is extended. The nature of the valency forces in the structure is considered, and it is suggested that cementite is essentially a framework of close-packed iron atoms held together by metallic bonding, with the small carbon atoms in the largest interstices, these atoms also being held in position by bonding which has a certain degree of metallic nature. This implies a close general resemblance to ferrite and austenite, and suggests that cementite may have many characteristics of a solid solution.

The possibility of variation in the cementite composition is considered, and experimental work on this point is described. Lattice-parameter variations are observed which appear to indicate composition variation.

The interpretation of the cementite structure is illustrated by applying it to the question of the influence of alloying elements on graphitisation.

## *Introduction.*

IN an earlier paper<sup>(1)</sup> with which the present author was concerned evidence of the positions of the carbon atoms in cementite was reported, thus completing that part of the determination of the cementite crystal structure left unsettled by the previous work of Westgren and Hendricks. There are certain features of this structure which, on account of the light that they throw upon the general nature of cementite, appear to merit fuller treatment than was accorded to them in the earlier paper.

Amongst those who are most interested in cementite it is usually regarded as having the characteristics of a true chemical compound, thus implying the formation of electrovalent or covalent bonding. The structure indicates, however, that this view requires some reconsideration, and it is proposed, therefore, to examine first of all the nature of the atomic bonding in cementite.

## *The Atomic Bonding in Cementite.*

The initial feature of the structure to which it is desired to draw attention is the fact that there must be direct iron-iron bonding. The details of the structure show that it cannot be held together by iron-carbon bonds only. The carbon atoms occur in the mirror planes, and in order to join the iron atoms which are associated with the carbon atoms in one plane to those associated with the carbon atoms in the next plane the assumption of iron-

\* Received December 14, 1943.

iron bonding becomes necessary. Each iron atom has a large number, 11 or 12, of practically equidistant iron neighbours, the interatomic separation being the same as that prevailing between the atoms in ferrite or austenite. The bond between the iron atoms must be essentially electrovalent, covalent or metallic, although no sharp line of demarcation exists between the three types. Electrovalent bonding between identical atoms is very improbable, and, assuming that each iron atom is bonded to all its neighbours, the large number of these indicates that normal covalency does not exist. There are, however, no such objections to metallic bonding, and the most reasonable conclusion would appear to be that the bond between the iron atoms is essentially metallic in nature.

For the iron-carbon bond electrovalency again appears improbable. It is difficult to see what ionic valency values the atoms would adopt, and, in addition, such bonding would mean that the iron-iron distances in the structure would involve the ionic radius of iron, so that the observed separation, which agrees with that found in metallic iron, would not be expected. Against the possibility of covalency is the fact that each carbon atom has six practically equidistant iron neighbours situated at the corners of a prism, whereas carbon has a covalency of only four, limited in direction to a tetrahedral distribution. It has been shown, however, that under certain conditions covalencies can resonate between a number of positions, and in the case of the simple carbides such as TaC, &c., where the carbon atoms again have six neighbours, Pauling<sup>(2)</sup> has suggested that such resonance does in fact take place. It appears possible, therefore, that this is the case in cementite. Such resonance represents a transition of the covalency towards a metallic nature. The only alternative iron-carbon bonding appears to be one of an even more metallic nature.

In cementite the actual disposition of the atoms is complex, but this interpretation of the bonding forces leads to the relatively simple picture of the structure consisting essentially of a framework of closely packed iron atoms held together by metallic bonding, with the small carbon atoms in the largest interstices, the carbon atoms also being held in position by bonding which has a certain amount of metallic nature, and the whole structure being more dominated by iron-iron than by iron-carbon bonding. In the previous paper on cementite it was pointed out that there was little resemblance in the detail of its structure to those of ferrite and of austenite. The present view, however, suggests a close general resemblance, all of them consisting of iron frameworks in the interstices of which carbon atoms are accommodated, and the iron-carbon bond probably being similar in each case. The conception of such a resemblance suggests, amongst other things, that, while cementite has normally attributed to it the nature of a chemical compound, a supposition supported by its

apparent constancy of composition, it is in fact to be expected that it will have many of the characteristics of a solid solution. The truth is probably that cementite illustrates the lack of a sharp line of demarcation between a solid solution and a compound; yet, on the whole, one may expect it to show properties which are more typically those of the former.

On this interpretation of the cementite structure it might be expected that the composition may not be exactly constant, and this is a conclusion which it appeared to be of interest to test experimentally.

### *The Composition of Cementite.*

Before proceeding to describe the experimental work on the variation in composition of cementite, it is desirable to examine the structure rather more closely from this point of view.

Where a structure is held together entirely by electrovalent or covalent bonding the valency relationships between the atoms must be satisfied, but in a structure such as cementite, where there is a closely packed framework of iron atoms joined together by metallic bonding, it seems possible that this framework may still exist even if, here and there, carbon atoms are missing from the interstices. In austenite, for example, the iron framework can exist even when carbon atoms are missing. The cause of the fairly constant composition of cementite then requires explanation. In the author's opinion this can be done in the following manner.

Cementite must be considered in relation to the other "interstitial structures," the carbides, nitrides and borides of the transition elements, which have been studied in detail by Hägg.<sup>(3)</sup> It would appear that in these structures the bonding forces demand close-packing of the atoms, and no limitation is imposed by the non-metallic atoms on the number or distribution of their metallic neighbours. Thus, the stable structure is simply the one which can achieve close-packing, and the stable composition is the one required to build this structure. This could happen only in structures dominated by metallic bonding and under circumstances where this bond demands close-packing in a manner similar to that in which it demands close-packing in face-centred cubic and close-packed hexagonal metals. All this is in contrast to electrovalent and covalent compounds, in which the valencies determine the composition, and the structure has then to accommodate this composition.

On this view the reason why a structure is found in the Fe-C system at the composition 3Fe : 1C is that with this composition it is possible to build a close-packed structure. It is not a valency requirement, and consequently, as already pointed out, some departure from this ratio would appear permissible. Great variation from 3Fe : 1C would not be expected. The usual type of composition variation arising from the replacement of one component

by another is not possible, on account of the difference in atomic size of iron and carbon. The most possible variation appears to be by omission of carbon atoms. The iron framework in cementite, however, is not the exact structure adopted by iron in the absence of carbon, so that, although the framework can probably continue to exist when a certain number of carbon atoms are missing, it would be expected that the extent to which this omission can take place would be rather limited.

These views are best understood when considered in terms of the free-energy/composition curves. For chemical compounds these rise very steeply from the minimum which occurs at the composition required by the valencies. Thus, in effect, only this one composition can exist. In the Fe-C system it is suggested that cementite occurs because of the low free-energy value associated with a close-packed structure, and it is also suggested that the minimum in the cementite free-energy/composition curve is at 3Fe : 1C, but the structure does not immediately become completely unstable on omission of carbon atoms, so that the free-energy curve rises much less steeply from the minimum than is the case with compounds. It has been shown that when two phases are in equilibrium their compositions depend upon the points of contact of the common tangent to the free-energy curves.<sup>(4)</sup> These views on the nature of the cementite free-energy curves therefore suggest the possibility that when cementite is in equilibrium with ferrite or austenite the point of contact of the common tangent, and therefore the equilibrium composition, will depart from 3Fe : 1C.

Experimental work to test this possibility has been carried out, and is described below. Schwartz<sup>(5)</sup> has reported a composition variation, but the amount appears improbably large. Variation has been established in the simple interstitial carbides in which the metal framework is not in general one which the metal atoms choose in the absence of carbon; this therefore represents a case closely parallel to cementite.

#### *Evidence of Composition Variation.*

If variation is possible the composition of cementite in equilibrium with the iron solid solution in a steel would be expected to vary with temperature. Cementites extracted from quenched hyper-eutectoid steels were therefore examined.

For this purpose a 1.8% carbon steel was made from pure iron (99.96%) and pure graphite (99.98%). These were melted together in a high-frequency furnace, using a magnesia crucible and a hydrogen atmosphere. The alloy was homogenised *in vacuo* at 1050° C. for 24 hr., and the surface layers were ground off. Finally, it was reheated *in vacuo* to 900° C., held there for 6 hr., and then slowly cooled at 20° C. per hr. to room temperature. This gave a coarse pearlite, so that there was no excessively fine cementite, and also gave a condition approaching room-temperature equilibrium,

although possibly rather remotely. The surface was very lightly reground, water-cooling being used, and the cementite extracted electrolytically in a 4% hydrochloric acid solution at a current density of about 20 milliamp. per sq. cm. After electrolysis the cementite was gently removed from the surface, well washed with cold dilute sodium carbonate solution, cold water, alcohol and ether, and finally dried. Similar extractions were made on the same alloy after quenching from various temperatures, the alloy being held 6 hr. *in vacuo* at each particular temperature. Micro-examination showed that in quenching from above the eutectoid line there was a tendency for considerable troostite formation around the undissolved hyper-eutectoid cementite, so that under these conditions not all the cementite extracted would be characteristic of the quenching temperature. Brine-quenching removed this difficulty. There was no trace of graphitisation during the heat treatments. Cementites from two other similar alloys were also studied.

An attempt was made to obtain analytical evidence of composition variation from the cementites produced in this manner. In spite of the precautions taken, the attempt was unsuccessful. Sufficient accuracy could not be obtained, on account of contamination of the cementite with free iron and carbon as a result of decomposition during extraction and subsequent treatment, and also as a result of the electrolytic decomposition of the martensite. The analyses merely showed that the compositions were in the 3Fe : 1C region. It became evident that to obtain any conclusion on the present point from analytical evidence would be a major problem. Although the analysis of cementite has been the subject of much published work, none of the methods would appear capable of giving a satisfactory solution.

Measurements were then made of the lattice parameters of the cementites, working on the assumption that any change in composition would be reflected in a change in parameter. These measurements proved more interesting than the analyses, the presence of free iron and carbon introducing no difficulty.

The extracted cementites gave sharp X-ray photographs. Cr  $K_{\alpha}$  radiation was employed with a 19-cm. camera,<sup>(6)</sup> calibrated by using the recently revised constants for quartz.<sup>(7)</sup> The parameters were estimated from the lines 140, 313, 025, 233 and 125. To correct for the systematic errors, approximate values of  $a$ ,  $b$  and  $c$  were assumed, and trial changes were then made until the differences between the observed and calculated values of  $\sin^2\theta$  for each reflection, when plotted against the  $\sin^22\theta$  value, lay on a straight line through the origin. Treatment of one set of readings by the least-squares method<sup>(8)</sup> proved more time-consuming than the above less elegant procedure.

The results of the parameter measurements are shown in Table I. Two separate determinations were made from each film.

These results appear to indicate that some variation in the Fe : C ratio in cementite is possible. It will be observed that there is a variation in the parameters with quenching temperature which, although small, is quite beyond the limits of experimental error. While the cementite is in equilibrium with ferrite the parameters remain practically constant; the variation is confined to the region of equilibrium with austenite. The variation is not erratic, but is systematic, and there is agreement between the three alloys used. This suggests that the cause is not a chance variation but a fundamental one.

TABLE I.—*The Change in the Lattice Parameters of Cementite with Quenching Temperature.*

Estimated accuracy  $\pm 0.0005 \text{ \AA}$ .

Alloy No.	Quenching Temp. °C.	Camera Temp. °C.	Lattice Parameter. Å.			Lattice Parameter Change. Å.		
			a.	b.	c.	a.	b.	c.
1	Room temp.	18.9	4.5139	5.0787	6.7292	0	0	0
1	400	18.9	4.5142	5.0788	6.7295	+0.0001	0	+0.0001
2	400	19.0	4.5139	5.0787	6.7291	+0.0003	-0.0002	+0.0003
1	680	20.2	4.5142	5.0785	6.7295	+0.0003	-0.0020	+0.0015
1	750	20.2	4.5119	5.0772	6.7309	+0.0003	-0.0015	+0.0017
2	850	19.0	4.5089	5.0742	6.7329	+0.0003	-0.0045	+0.0037
3	850	19.0	4.5089	5.0742	6.7329	+0.0003	-0.0045	+0.0037
1	900	21.0	4.5069	5.0735	6.7339	+0.0003	-0.0052	+0.0047
2 *	900	22.4	4.5074	5.0735	6.7339	+0.0003	-0.0052	+0.0047
2 *	900	19.0	4.5074	5.0735	6.7339	+0.0003	-0.0052	+0.0047

\* Different films.

It might be suggested that the lattice-parameter changes could be explained as being due to quenching stresses, but, unless the cementite was plastically deformed, the effect of quenching stresses would be removed by extraction from the iron. Since the samples gave sharp X-ray lines there could have been little plastic deformation. Moreover, if there were any residual stresses, their value in any particular plane would depend upon the orientation in the original quenched lump. After extraction the cementite particles are randomly orientated, so that each line in the X-ray photograph is made up of spots from planes which would be subjected to various amounts of residual stress. If the stress were sufficient to cause appreciable displacement of the diffracted beams, the displacement would be different for each spot, and very diffuse lines would result.

Composition appears to be the only variant which could produce the observed results, but the composition variation might be in dissolved impurity and not in the Fe : C ratio. It will be remembered, however, that very pure iron and carbon were used in these alloys, and there appears no reason for great impurity pick-up during melting. The amount of the lattice-parameter change

seems too large to be due to iron replacement by small amounts of impurity, particularly since replacement could only take place to any marked extent by elements close in atomic size to iron. It is not, however, really possible to estimate what amount of a particular impurity would have to be present to produce a certain parameter change. For example, in the case of chromium, for which measurements are available, the cementite cell contracts although the entering element is larger than iron.<sup>(9)</sup> To test for impurity variation spectrographic analyses were made of samples of cementite extracted after quenching from 400° C. and 900° C. No significant difference could be found between the two samples. The only impurities detected at all were very slight traces of magnesium, nickel, silicon and zinc. Nitrogen and hydrogen are elements which may be able to enter cementite, and they would not be detected spectrographically, but it is hard to see how there could be any nitrogen pick-up, and, although the alloys were melted in hydrogen, they were subsequently annealed for a long time *in vacuo* at 1050° C. Explanation of the results in terms of impurity would thus seem to be eliminated, and this is supported by the agreement between the measurements for the three alloys used. It is felt, therefore, that the most reasonable explanation is in terms of small variations in the Fe : C ratio.

It is concluded that the lattice-parameter variations would seem to indicate that composition variation in cementite is possible. This conclusion indirectly supports the views which have been advanced on the valencies present in the structure and on the reason for its existence at 3Fe : 1C.

### *The Graphitisation of Cementite.*

It is proposed to illustrate very briefly the results which can be deduced from this interpretation of the cementite structure by referring to the process of graphitisation. The presence of alloying elements in a steel or cast iron has a profound effect on this process, and, while in many cases the cause of this effect is still obscure, in others the alloying elements act by becoming part of the cementite structure. This can be achieved by the entering element replacing iron or carbon atoms or occupying some new site.

First of all, consider the possibility of replacement of iron atoms. If cementite were a truly covalent or electrovalent substance, iron could be replaced only by elements of the same valency, and only by these if they were of similar atomic size. In the actual cementite structure, however, it would appear possible to alloy the framework of metal atoms in exactly the same way as it is possible to alloy the frameworks in ferrite and austenite. Thus, the conditions for replacement of iron in cementite become the general conditions for substitutional solid-solution formation.

These merely require that the atoms do not differ by more than about 15% in atomic radius and are not too chemically dissimilar.

From this it can be understood how manganese and chromium can replace iron in cementite; it is simply because of the similarity of their atomic size to that of iron. The question of valency does not arise. By their entry they stabilise cementite, but with elements such as titanium, tantalum, zirconium, &c., it is immediately possible to say that they cannot behave in this manner, because their atoms are too large to replace iron. Similarly, with vanadium, tungsten and molybdenum it follows that, although replacement is not forbidden by atomic size, it will not take place as readily as with manganese and chromium. It must be realised that when the size factor is favourable for entry into cementite it is also favourable for entry into ferrite and austenite, and in a steel or cast iron the actual free-energy values may favour the accommodation of the alloying elements in these phases rather than in cementite. In general, the ferrite or austenite is actually preferred, although chromium supplies a notable exception.

Replacement of carbon would also seem possible under rather similar conditions, the resonance of the covalent bonds relaxing the valency limitation. Nitrogen is the only possible element from the point of view of atomic size, but there is no experimental evidence of actual replacement available, although such replacement can take place in TiC. Another possibility is solubility of hydrogen, the interstices smaller than those occupied by carbon being used. Again no experimental evidence is available.

In the industrially important hard carbides the same principles as in cementite will apply to atomic replacement.

These points indicate that this interpretation of the structure of cementite permits the appreciation of certain aspects of its metallurgical behaviour.

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# FACTORS AFFECTING THE STRENGTH OF SOLDERED JOINTS MADE FROM ELECTRO- TINNED STEEL SHEET.<sup>1</sup>

By A. W. HOTHERSALL, M.Sc., D. W. HOPKINS, B.Sc., AND  
G. L. EVANS, B.Sc.

## SUMMARY.

The effect of the method of cleaning steel sheet in preparation for electro-tinning on the strength of soldered joints has been investigated, using a tearing test. The effect on the joint strength of the weight of tin coating, the time of storing the plated sheet before soldering and the type of solder were also examined.

The method used for cleaning the steel sheet in preparation for electro-tinning had a marked effect upon the strength of the soldered joint as determined by a tearing test, especially when an acid tin bath was employed. With the acid bath the type of cleaning cycle ordinarily used in electroplating practice gave low joint strengths, and the initially low strength further decreased appreciably on heating the plated sheet before soldering to the temperature required for stoving tinplate lacquers. It was found that by treatment in an alkaline solution after pickling and immediately before plating in the acid bath joint strengths were markedly improved and no loss in strength was produced by stoving the plated sheets before soldering. Methods of applying this discovery to the electro-tinning of sheet were investigated, and suitable procedures are indicated.

Using this pretreatment in alkaline solution, joint strengths for any given steel sheet and method of pickling were closely similar with the acid electrolyte to those obtained with the sodium stannate bath and were at least equal to those given by hot-dipped tinplate made from similar steel.

Joints soldered after storage of the electro-tinned sheet were less strong than when the sheet was freshly tinned. With dry storage the strength fell in sixteen weeks by 10% (sodium stannate bath, 4-oz. coatings) and 15% (acid tin bath, 4-oz. coatings, with pretreatment in alkali). The deterioration in joint strength was more rapid when soldering followed storage in a corrosive atmosphere.

Soldered joints increased in strength on keeping for sixteen weeks, the amount of the increase varying with solder containing 40% of tin from 6% to 30%, according to the conditions of electro-tinning. With solder containing 60% of tin the increase was greater (up to 70%).

## INTRODUCTION.

THERE are, especially in time of war, a variety of containers made by soldering thin sheet steel which is lacquered or painted before or after fabrication; such material often only needs protection from rusting between the time of manufacture at the steelworks

<sup>1</sup> Communication from the Armament Research Department (formerly the Research Department, Woolwich), received November 26, 1943.

and use at the box-making factory, and the chief function of a tin coating is then to assist soldering in box-making.

As well as providing an airtight seal, the soldered joints must be strong, as they are often subjected to stress. If the sheet is lacquered before being made into containers the stoving after lacquering must not adversely affect the soundness or the strength of the subsequently soldered joint.

It was understood from results of American experience in the use of electro-tinned strip that steel electroplated with 6-8 oz. of tin per basis box, instead of the 20-24 oz. per basis box present on hot-dipped tinplate, could be made into cans and containers without difficulty, although some difficulty with low strength on soldering after lacquering has been suggested. There are many important differences between the conditions to be met in electro-tinning sheet and strip, however, and the work described in this paper was done primarily with the object of establishing a procedure for the electro-tinning of steel sheet which would enable strong soldered joints to be made.

#### METHOD OF TESTING JOINT STRENGTH.

In the early stages of the work, tests of solderability were made on automatic can-making machines with the co-operation of the National Oil Refinery and the Metal Box Company, Ltd., to whom acknowledgment is made for their helpful co-operation. Examination of the containers made on these machines (including seam strengths) was correlated with the results of a laboratory test of joint strength based on the Chadwick test,<sup>1</sup> and general agreement was found. This laboratory test was further developed, as it enabled a quantitative comparison to be made quickly of samples produced under a variety of conditions. Whilst it is not suggested that this tearing test of soldered joints is an adequate method of assessing the solderability of tinned sheet, it has been found that, when carefully standardised, it provides a delicate method of comparing the effect of changes in cleaning procedure before electro-tinning on the strength of a subsequently soldered joint. It remains to be proved that conditions of electro-tinning which give strong joints in this test necessarily do so in production, but the preliminary results referred to above suggest that there is some agreement.

A description of the method of testing is given in an Appendix.

#### SCOPE AND METHOD OF INVESTIGATION.

##### *The Test Samples.*

The test samples consisted of can-body blanks, 9·4 × 4·8 in. in size, cut from steel sheet, 0·010-0·011 in. in thickness. These specimens were plated in a jig so designed as to give a tin coating of reasonably uniform thickness. Uniformity was tested by com-

<sup>1</sup> R. Chadwick, *Journal of the Institute of Metals*, 1938, vol. 62, p. 277.

paring the tin yield on  $\frac{1}{4}$ -in. wide strips, cut from the edge of the blank, with the average for the whole sheet. When these values differed by not more than 0.5 oz. per basis box<sup>1</sup> (*i.e.*,  $1.8 \times 10^{-6}$  in. thickness or 12.5% of the thickness of coating normally applied in this work) distribution was considered satisfactory.

Joint-strength values quoted refer, unless otherwise stated, to samples coated in the acid tinplating bath with 4 oz. of tin per basis box, and are related in some Tables to the joint strength of tinplate made from pack-rolled and box-annealed sheet taken as 100. This method of expressing the results was adopted because of differences found in the strength of joints made both with hot-dipped tinplate and with electro-tinned steel using steel from different sources.

An investigation of the following factors was made :

- (1) The preparation of the steel base before plating.
- (2) The choice of tin bath, acid or alkaline.
- (3) The effect of the weight of the tin coating.
- (4) The effect of ageing plated sheets before soldering.
- (5) The effect of heating to the stoving temperature of the lacquering oven.
- (6) The effect of ageing on the strength of soldered joints.
- (7) The choice of the type of solder.

#### *The Tinplating Baths.*

##### *Acid Tinplating Bath.*

The acid tinplating bath developed by Hothersall and Bradshaw<sup>2</sup> was first used (bath No. 1) and the results were compared

TABLE I.—*Acid Tinplating Baths.*

	Bath No. 1. G. per litre.	Bath No. 2. G. per litre.
Stannous sulphate crystals . . .	55	25
Sulphuric acid . . . .	50	50
Cresol sulphonic acid . . . .	100	20
$\beta$ -Naphthol . . . .	1	1
Gelatine . . . .	2	2

with those obtained with bath No. 2 (reduced concentrations of tin and cresol sulphonic acid for economy). No difference in joint strength was found, and the majority of the work was done with bath No. 2. The compositions of the baths are given in Table I.

<sup>1</sup> A basis box of tinplate contains 112 sheets,  $14 \times 20$  in. in size, the surface area, counting both sides, being 62,720 sq. in. 1 lb. of tin per basis box if evenly distributed would be equivalent to a thickness of 0.000059 in. "Coke" grades of tinplate normally carry 16–22 oz. of tin per basis box.

<sup>2</sup> *Journal of the Electrodepositors' Technical Society*, 1937, vol. 12, p. 113; 1939, vol. 15, p. 31.

*Conditions of Use.*—The acid tinplating bath was used under the following conditions :

Room temperature.

Current density, 20 amp. per sq. ft. (= 0.001 in. in 25 min. or 4 oz. per basis box in 22.5 sec.).

No agitation.

#### *Alkaline Sodium Stannate Bath.*

The particular objective of this work was to investigate the use of the acid tinplating bath for the coating of steel sheet. Comparative tests were made with an alkaline sodium stannate bath. As the number of tests required to be made with this bath was small, it was used with insoluble anodes for convenience of operation.

*Composition.*—The following was the composition of the sodium stannate bath :

Sodium stannate : 100 g. per litre.

Sodium hydroxide : 20 g. " "

*Conditions of Use.*—The bath was used under the following conditions :

Temperature, 75° C.

Current density, 15 amp. per sq. ft. (= 0.001 in. in 75 min. or 4 oz. per basis box in 67.5 sec.).

No agitation.

#### METHOD OF PREPARATION OF STEEL SHEET FOR PLATING.

The basis metal used throughout this portion of the investigation was pack-rolled box-annealed blackplate, though parallel experiments were in some cases carried out on other material.

Steel sheet as received from white annealing was subjected to various conditions of pickling in sulphuric acid solutions, rinsed and plated with tin in either the acid or alkaline tinplating bath. The time and temperature of pickling and the concentration of the acid were found to affect the strength of subsequently soldered joints, but with ordinary pickling the maximum strength of joint obtained with samples plated in the acid tin bath was only 60–63% of that of hot-dipped tinplate (with the samples used, the optimum conditions of pickling were : 5%  $H_2SO_4$  by weight with inhibitor, 45° C., 30 sec.). Typical results are compared in Table II.

A considerable improvement was produced by using the method of cleaning steel which has been found to give very strongly adherent deposits of nickel, viz., anodic treatment at high current density (200 amp. per sq. ft.) in a 30% solution of  $H_2SO_4$  by weight. This treatment resulted in joint strengths comparable with those given by hot-dipped tinplate.

Vigorous scrubbing of the sheets after chemical pickling, with the object of removing any film of detritus (*e.g.*, of carbon, carbides or resistant oxides), raised the joint strength value to 85–90% of that given by hot-dipped tinplate. Storage of the pickled sheets in a dilute solution of hydrochloric acid (0·25–4% of concentrated acid by volume), a process known in the trade as “sweetening,” raised the joint strength value to that of hot-dipped tinplate with the particular samples tested.<sup>1</sup>

TABLE II.—*Effect of Cleaning Treatment before Tinplating on Strength of Soldered Joints.*

Solder : 60% tin, 40% lead.

Cleaning Treatment.	Relative Joint Strength.	
	Acid Tin Bath.	Sodium Stannate Bath.
(1) Pickle 5% H <sub>2</sub> SO <sub>4</sub> , 5 min. at 75° C., rinse . . .	53	...
(2) Pickle 5% H <sub>2</sub> SO <sub>4</sub> , 30 sec. at 45° C., rinse . . .	61	98
(3) Pickle as (2), 1–30 sec. dip in alkali at 75° C., rinse . . . . .	105	99
(4) Pickle as (2), brushed, rinse . . . . .	87	119
(5) Anodic treatment in 30% H <sub>2</sub> SO <sub>4</sub> , 90 sec. at 200 amp. per sq. ft. . . . .	104	125
(6) Anodic treatment as (5), hot alkali as (3) . . . . .	125	125
(7) Pickle as (2), dip 5 min. in alkali at 20° C. . . . .	104	98
(8) Pickle as (2), dip 1 hr. in 5% Na <sub>2</sub> CO <sub>3</sub> at 20° C. . . . .	105	98
(9) Pickle as (2), stored 1% HCl, 1 hr. cold alkali as (7) . . . . .	125	125
(10) Pickle as (2), cathodic alkali 20 sec. at 75° C. . . . .	104	...
(11) Pickle as (2), anodic alkali 20 sec. at 75° C. . . . .	105	...
(12) Hot-dipped tinplate . . . . .	100	

All of the above results were obtained with the acid tinplating bath. With the sodium stannate bath all samples had a higher joint strength, the lowest result obtained being comparable with those given by tinplate and the highest being up to 50% greater than with tinplate.

#### COMPARISON OF ACID AND ALKALINE TINPLATING BATHS.

The cause of the stronger joints obtained with the sodium stannate bath was first examined by electro-tinning steel with composite coatings built up partly in the acid and partly in the alkaline bath. Stronger joints were always obtained if the cleaned steel was plated first in the sodium stannate bath. The relative

<sup>1</sup> The authors are indebted to Mr. D. Luther Phillips for this suggestion.

thicknesses of tin in each bath made little or no difference to the joint strength.

It was subsequently found that dipping the cleaned steel into an alkaline solution gave the same result as pre-plating in the sodium stannate bath.

The results given in Table II. were obtained at different times with different samples of steel; blank tests using a standard cleaning treatment enabled comparative values to be calculated. Typical results of actual joint strengths can be calculated from the

TABLE III.—*Effect of Method of Cleaning, Plating Bath and Type of Steel on Joint Strength.*

4-oz. tin coating. Thickness of sheet: 0·01–0·0105 in. Solder: 40% tin, 60% lead.

Steel Sheet.	Plating Bath.	Joint Strength. Lb.			
		Cleaned by Pickle in $H_2SO_4$ .		Cleaned by Anodic Treatment in 30% $H_2SO_4$ .	
		N.A. <sup>*</sup>	A. <sup>†</sup>	N.A. <sup>*</sup>	A. <sup>†</sup>
Hot-rolled sheet	Acid	20·5	35	34·5	41·5
	Stannate	32·5	33	42	41·5
Cold-rolled strip	Acid	31	37·5	40	46·5
	Stannate	37·5	37·5	46·5	46·5

\* N.A. = Not dipped in alkaline solution after acid cleaning.

† A = Dipped in alkaline solution after acid cleaning.

figures in Table II. by using the average value for the joint strengths obtained with pack-rolled hot-dipped tinplate of 30 lb. (range with different materials, 27–32 lb.). Higher figures for joint strength were obtained with cold-rolled sheet. Examples of actual results with both pack-rolled sheet and cold-rolled strip are given in Table III.

TABLE IV.—*Effect of Time of Delay in Acid Tinplating Bath before Applying Current.*

Solder: 40% tin, 60% lead.

Delay before Plating. Sec.	Relative Joint Strength.
0	105
5	104
10	97
20	91
30	71
60	61
Hot-dipped tinplate	100

The cause of the beneficial effect of dipping in alkaline solution was next examined and it was found that if a piece of pickled steel, dipped in alkaline solution and washed, was held in the acid plating solution for various times before switching on the current, the strength of a subsequently soldered joint decreased in proportion to the time of delay before switching on the current. The results are shown in Table IV.

It was supposed that the loss of joint strength was due to the adsorption of gelatine from the acid plating solution, which occurs more readily in an acid medium (*i.e.*, more acid than pH 4·9, the iso-electric point of gelatine). This supposition was confirmed by dipping pickled and brushed steel sheet into solutions of gelatine (containing 2 g. of gelatine per litre) at pH 3 and pH 7 (obtained by adding sulphuric acid or sodium hydroxide) for 30 sec. and then plating in the acid bath. The sheet dipped into the solution at pH 7 gave a joint strength 50% greater than that dipped into the acid gelatine solution. In order to eliminate any possible interference by detritus left on the surface of the steel after pickling, the experiment was repeated using copper foil (cleaned by a short dip in 50% HNO<sub>3</sub>) and electrolytic iron sheet; similar results to those obtained with steel sheet were recorded.

Additional evidence was obtained by plating sheets in acid baths containing less than the normal quantity of addition agent; the pre-cleaning treatment was in all cases anodic passivation in 30% solution of H<sub>2</sub>SO<sub>4</sub> and a 4-oz. per basis box coating was deposited throughout. The results are recorded in Table V.

TABLE V.—*Effect of Concentration of Addition Agents on Joint Strength.*

Solder : 60% tin, 40% lead.

Addition Agent. G. per litre.		Joint Strength of Plated Sheet.	
Gelatine.	$\beta$ -Naphthol.	Lb.	Relative Values.
...	...	41·5	125
0·5	0·25	40·5	123
1·0	0·5	39	118
1·5	0·75	35	106
2·0 *	1·0 *	33	100

\* Normal bath.

It would appear that clean steel sheet treated in alkaline solution is left with a film of alkaline liquid held in pores in the surface or by any solid film—for example, of residues from pickling—and that this alkaline film retards adsorption of gelatine by the steel base until deposition of tin has commenced. This discovery has been covered by patent application.<sup>1</sup>

#### CLEANING CYCLE FOR USE IN PRODUCTION TINNING OF STEEL SHEET.

By the use of an alkaline dip before electro-tinning in the acid bath, it was found practicable to make use of the ordinary white-

<sup>1</sup> British patent application No. 15324/42.

pickling plant available in tinplate works, thus saving the expense, material and extra space needed for a special cleaning unit attached to the electro-tinning plant. The recommended method is to wash the sheets from the pickle, dip them into a 5% solution of soda-ash, wash and plate with tin; alternatively, they may be washed and stored in a bosh containing a very dilute solution of soda-ash (say, 0·5%), from which they are taken direct to the tinplating tank.

This method should, however, be recognised as a make-shift, and it is desirable where possible to arrange for a cleaning unit to be incorporated in line with the plating, so that sheet from the white anneal may be put, dry, into the loading end of the plant and removed, plated, from the delivery end. To avoid the installation of a lengthy series of cleaning tanks, it is necessary to evolve a method capable of treating sheet with blue edges, and possibly having greasy finger-prints, in the time necessary to deposit the minimum weight of tin coating likely to be required. The shortest time that could be envisaged as available for each cleaning treatment was 10 sec., and after trial of various procedures the following cleaning cycle was developed as suitable for thoroughly cleaning sheets specially selected as having deep blue edges; the maximum current available for cleaning operations was taken as 30 amp. per sq. ft. in each bath :

#### *Stage 1.—Electrolytic Alkali Treatment.*

*Objects.*—To remove grease, finger-prints, &c.; to wet the surface thoroughly, so that subsequent attack by acid might remove oxide in the shortest possible time.

*Results.*—The most satisfactory method tried was anodic treatment in alkaline solution containing 100 g. of sodium hydroxide and 100 g. of sodium carbonate per litre, at a temperature of 70° C. and current density of 20 amp. per sq. ft. Less concentrated solutions at a lower temperature were not effective in the time available. For some reason not at present clear, cathodic treatment was less effective than anodic in obtaining a clean sheet after stage 3.

#### *Stage 2.—Acid Pickling.*

*Objects.*—To remove oxides from the surface, leaving as little loose solid material on the surface as possible.

*Conditions Tried.*—Sulphuric acid and hydrochloric acid, in concentrations up to 20%, and at temperatures up to 70° C., with and without electrolysis (anodic or cathodic).

*Results.*—Sulphuric acid was not effective in the time available. Satisfactory results were obtained with hydrochloric acid (20% of concentrated acid solution by volume) at a temperature of 70° C., without electrolysis.

*Stage 3.—Alkali Pretreatment.*

*Objects.*—To fill surface crevices with alkaline liquid and if possible also to remove any solid film left after acid pickling.

*Results.*—Satisfactory results were obtained with a duplication of the treatment used for stage 1. The conditions are not believed to be critical, and it is thought probable that electrolysis and the use of a high temperature in this treatment could be sacrificed without much loss of efficiency. These possibilities have, however, not been fully investigated, but, judging by the appearance of the sheets, anodic treatment in hot alkali was advantageous compared with simple immersion.

The recommended method was tried out on steel specimens cut from the same hot-rolled sheet, 28 × 30 in. in size, and was compared with other methods of cleaning. The following results were obtained, using solder containing 40% of tin and 60% of lead :

	Joint Strength. Lb.
(1) Cleaned and electro-tinned under commercial conditions, using alkali pretreatment . . . . .	31.5
(2) Cleaned in laboratory by similar method, but without pretreatment in alkali . . . . .	27
(3) Cleaned by method recommended above for production tinning . . . . .	33.5

Steel sheets 20 × 14 in. in size were also treated successfully, samples cut from them giving an average joint strength of 32 lb. (range, 30.5–34 lb.).

#### THE EFFECT OF THE WEIGHT OF THE TIN COATING ON THE STRENGTH OF SOLDERED JOINTS.

The effect of the weight of tin coating on the strength of the soldered joint was examined by the plating of steel sheets in both the acid tin and sodium stannate baths with deposits of 2, 4, 6, 8

TABLE VI.—*Effect of Weight of Tin Coating on Strength of Soldered Joints.*

Solder : 60% tin, 40% lead.

Tin Coating. Oz. per basis box.	Relative Joint Strength (Averages of Numerous Tests).		Typical Results of Joint-Strength Tests. Lb.	
	Acid Bath.	Sodium Stannate Bath.	Acid Bath.*	Sodium Stannate Bath.†
2	95	95	28.5	38
4	100	100	29.5	39.5
6	94	96	26.5	38.5
8	87	89	25.5	36
20	81	81	24	31.5

\* No pretreatment in alkaline solution; pack-rolled sheet.

† Cold-rolled strip.

and 20 oz. per basis box. As shown in Table VI., deposits of 4 oz. per basis box gave the maximum joint-strength values. The composition of the solder was 60% tin, 40% lead; the sheets were prepared for plating in the acid tin bath by pickling in a warm 5% sulphuric acid solution, rinsing and brushing.

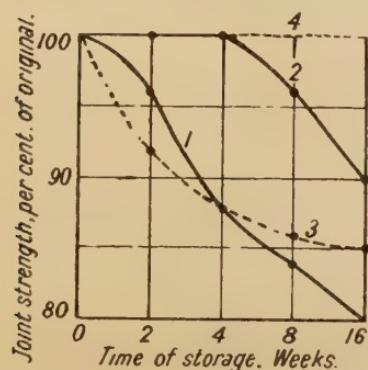
The effect of the weight of tin coating was not examined with variations in the soldering conditions, such as the time of dipping and temperature and the composition of the solder bath.

#### THE EFFECT OF CORROSION OF THE ELECTRO-TINNED SHEET ON THE STRENGTH OF SOLDERED JOINTS.

In one series of tests, made before the discovery of the advantage of pretreatment in alkaline solution, steel sheets were prepared

for plating by degreasing and pickling in 5%  $H_2SO_4$  solution at 45° C. for 5 min., followed by brushing with a bristle brush, rinsing and plating (cleaning treatment 1). In a later series, the same cleaning treatment was used, but was followed by dipping for 1 min. in a 1% solution of sodium carbonate and rinsing (cleaning treatment 2).

The sheets were plated with various weights of tin coating equivalent to 2 to 20 oz. per basis box. Specimens were then exposed under each of the following conditions :



- Curve 1.—Acid bath; no alkali pretreatment.
- Curve 2.—Stannate bath.
- Curve 3.—Acid bath; alkali pretreatment.
- Curve 4.—Hot-dipped tinplate, 20-oz. coating.

FIG. 1.—Effect of Method of Plating on Strength of Soldered Joint made after progressive times of storage in a desiccator. (Electro-tinned coatings, all 4 oz.)

ends 3 in. above a layer of water covering the bottom of the container.

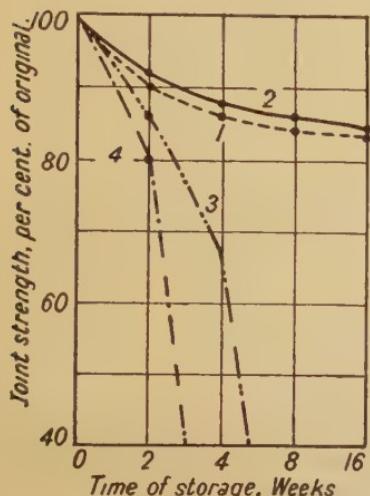
Visual examinations at weekly intervals were made to determine the rate of formation of rust. Samples were also taken from sets A and B for joint-strength determinations after periods of 1, 2, 4, 8 and 16 weeks. With set B, the soldered faces of the joints were those which had been uppermost during exposure and which

A.—Stored in a desiccator.

B.—Exposed horizontally in an unheated lean-to with corrugated-iron walls and adjacent to pickling and plating operations (November–February).

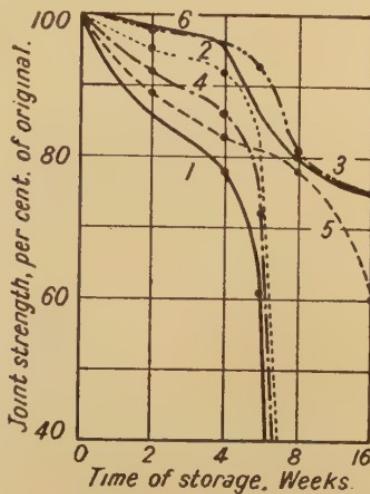
C.—Hung vertically in a covered container with the lower

corroded much more rapidly than the underneath faces; the specimens were not cleaned before soldering; the solder used contained 60% of tin and 40% of lead. The plates corroded appreciably during the 16 weeks' exposure, the first signs of rust being noticeable in 2-11 weeks, according to the thickness of coating and the conditions of electro-tinning. Judging by appearance, coatings



- Curve 1.—8-oz. coating; storage in desiccator.
- Curve 2.—4-oz. coating; storage in desiccator.
- Curve 3.—8-oz. coating; storage in corrosive atmosphere.
- Curve 4.—4-oz. coating; storage in corrosive atmosphere.

FIG. 2.—Effect of Conditions of Storage on Strength of Soldered Joints (sheet pretreated in alkaline solution and electro-tinned in the acid bath).



- Curve 1.—Acid bath, 4-oz. coating.
- Curve 2.—Acid bath, 8-oz. coating.
- Curve 3.—Acid bath, 20-oz. coating.
- Curve 4.—Stannate bath, 4-oz. coating.
- Curve 5.—Stannate bath, 8-oz. coating.
- Curve 6.—Hot-dipped tinplate, 20-oz. coating.

FIG. 3.—Effect of Weight of Tin Coating on Strength of Soldered Joints made after progressive times of storage in a corrosive atmosphere (acid-bath coatings, no alkali pretreatment).

from the acid bath were in general inferior in protective value to those made in the sodium stannate bath, rust being observable sooner and corrosion appearing to proceed at a somewhat more rapid rate. The rate of deterioration of the specimens did not appear to differ much between the two conditions of exposure *B* and *C*; only specimens from series *B* were soldered. Results of tests of joint strength are indicated in Figs. 1, 2 and 3. After

appreciable corrosion, the joints were too weak to test and a value of 0 was returned.

Examination of the results indicated the following conclusions :

(a) Without alkali pretreatment, the deposits from the acid bath offered less protection than those from the sodium stannate bath. Under non-corrosive conditions the joint-strength value fell on storage, irrespective of the thickness of coating (up to 16 oz. per basis box). Deposits from the sodium stannate bath showed this effect less than those from the acid bath.

(b) The resistance to corrosion was very low with tin coatings lighter than 4 oz. per basis box, plated in either the acid or the sodium stannate bath.

(c) The introduction of an alkaline pretreatment immediately before deposition in the acid bath decreased the amount of corrosion on standing and improved the solderability of the plated sheet.

#### THE EFFECT OF HEATING ELECTRO-TINNED SHEETS TO THE LACQUERING TEMPERATURE.

Experiments were conducted to determine the effect on joint strength of heating electro-tinned steel sheet to temperatures corresponding to those used in stoving lacquered sheets. The heat

TABLE VII.—*Effect of Heating before Soldering on Joint Strength.*  
Solder : 40% tin, 60% lead.

Plating Bath.	Pre-Plating Treatment.	Change in Joint Strength after Heating to 200° C. for $\frac{1}{2}$ hr.
(1) Acid	Anodic in 30% $H_2SO_4$ , 90 sec., 200 amp. per sq. ft.; rinse.	Loss, 30%
(2) Acid	5 min. pickle in 5% $H_2SO_4$ at 45° C.; brush and rinse.	Loss, 30%
(3) Acid	Pickle as (2), 5 min., dip in 0.5% $Na_2CO_3$ , 20° C.; rinse.	Gain, 2%
(4) Stannate	Anodic passivation as (1)	Gain, 1%
(5) Stannate	Pickle and brush as (2)	Gain, 2%
Hot-dipped tinplate		Gain, 6%

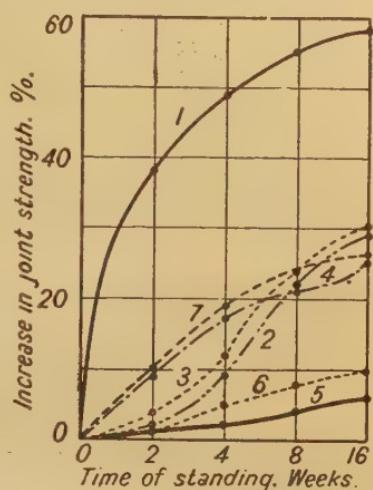
treatment used in this investigation was to maintain the specimens at 190–200° C. for 35 min.

Steel sheet electro-tinned in the sodium stannate bath behaved similarly to hot-dipped tinplate, i.e., the joint strength of the heated sheet was equal to, or slightly greater than, the original joint strength.

The effect of heat treatment on the joint strength of sheet plated in the acid tin bath was found to be dependent upon the pre-plating treatment. Steel sheet cleaned by various methods of pickling in sulphuric acid but without final treatment in an alkaline solution showed a marked decrease in joint strength after heat treatment. If, on the other hand, the steel was dipped in an alkaline solution immediately before plating, the tinned sheet behaved on heating in the same way as tinplate or sheet plated in the sodium stannate bath. The results are recorded in Table VII.

#### THE EFFECT OF AGEING SOLDERED JOINTS.

Joints were made with steel sheet tinned both by hot-dipping and by electroplating in acid and alkaline baths and were allowed to stand at room temperature in a non-corrosive atmosphere for several weeks, specimens being withdrawn at intervals for testing. The results are shown in Fig. 4. Irrespective of the method of cleaning or tinning the steel or of the solder used, the joints increased in strength on standing. The weight of tin coating on the steel had little effect; sheets with 2 oz. of tin per basis box gave almost identical increases in strength on standing to those with 4 and 8 oz. Sheets plated in the sodium stannate bath showed a much greater increase in strength than hot-dipped tinplate or than specimens plated in the acid bath without pretreatment in alkali. Specimens treated in alkali before plating in the acid bath gave similar results to those plated in the sodium stannate bath.



Curves 1 to 3.—Solder, 60% tin, 40% lead.

Curve 1.—Stannate bath.

Curve 2.—Acid tin bath (no alkali pretreatment).

Curve 3.—Hot-dipped tinplate.

Curves 4 to 7.—Solder 40% tin, 60% lead.

Curve 4.—Stannate bath.

Curve 5.—Acid tin bath (no alkali pretreatment).

Curve 6.—Hot-dipped tinplate.

Curve 7.—Acid tin bath (alkali pretreatment).

FIG. 4.—Effect of Time of Standing after Soldering on Strength of Joints. (Electro-tinned coatings, all 8 oz.; hot-dipped coatings, 20 oz.)

#### COMPARISON OF VARIOUS SOLDERS.

Joint-strength determinations were made with the following solders :

- (a) 40% tin, 60% lead.
- (b) Argent solder T280.
- (c) Argent solder Q250.
- (d) Lead-silver solder, *S* eutectic.

Each solder was heated to 50° C. above its liquidus temperature.

Three varieties of tinned sheet were used, namely :

- (i) Hot-dipped tinplate.
- (ii) Electro-tinned sheet prepared for plating by pickling for 3 min. at 45° C. in 5%  $H_2SO_4$ , rinsing, dipping for 5 min. in a 0.5% solution of sodium carbonate, and plating in the acid bath No. 2 with a tin coating of 2 oz. per basis box.
- (iii) Electro-tinned sheet prepared as (ii) but coated with 8 oz. per basis box.

The results are shown in Table VIII., in which the joint-strength values are related to that of hot-dipped tinplate joined with lead-tin solder (60 : 40) as an index of 100 (joint-strength, 30 lb.).

TABLE VIII.—*Relative Joint Strength obtained with Various Solders.*

Tin Coating.	Relative Joint Strength with Solder named :			
	40% Tin, 60% Lead.	Argent T280.	Argent Q250.	Lead-Silver <i>S</i> .
(i) Hot dipped . .	100	105	90	140
(ii) Electrolytic, 2 oz. . .	110	120	110	145
(iii) Electrolytic, 8 oz. . .	115	120	110	145

Joints made with these solders were allowed to stand and were tested at intervals up to 16 weeks. The joints all increased in strength, the rate and amount of the increase being not greatly different for the various solders; after storage for 16 weeks the maximum increase was 33% (Argent T280) and the minimum increase 25% (lead-tin solder).

#### ACKNOWLEDGMENT.

Acknowledgment is made to the Director-General of Scientific Research and Development, Ministry of Supply, for permission to publish this paper.

#### APPENDIX.—*The Method Used for Testing the Strength of Soldered Joints.*

A laboratory method of determining joint strength was needed which would fulfil the following requirements :

- (1) The test must be rapid; when investigating pickling

conditions, for example, several variants were involved, which resulted in a large number of samples.

(2) Small differences of joint strength must be detectable by the test.

The method eventually devised and adopted was evolved with these considerations in mind. Though not a precision test, it was capable of producing results sufficiently accurate to enable differences in joint strength of 10% to be detected.

In order to obtain consistent results in determining the strength of soldered joints, it is essential that :

- (1) The thickness of the joint should be constant throughout a series of determinations.
- (2) The temperature of the solder bath in which the joint is made should be under accurate control.
- (3) The period of immersion in the solder bath should be standardised.

In practice, these considerations require the members of the joint to be kept parallel and at a known distance apart during immersion in the solder, and make it necessary to ensure that the total heat capacity of the jointed members together with the apparatus used to keep them in position is as small as possible.

*Preparation of the Joint.*—Strips of tinned steel  $2\frac{3}{4} \times 1$  in. in size were cut and flattened in a vice between lead foil. Aluminium foil (1 in. wide, 0.0065 in. thick) was folded over both ends of one

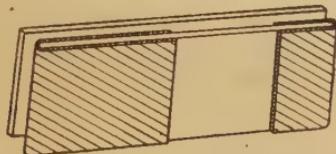


FIG. 5.—Preparation of Joint.

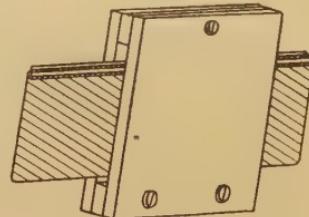


FIG. 6.—Jig for making Soldered Joint.

member of the joint as in Fig. 5 (aluminium being shown shaded) so that approximately 1 in. of the tinned strip remained uncovered. This portion and a corresponding portion of the opposite member of the joint were then fluxed, generally with zinc-ammonium chloride solution, before insertion in the joint-making jig.

The jig used in making the soldered joint is shown in Fig. 6 with the members of the joint in position. It consisted of two Duralumin plates  $1\frac{1}{2} \times 2 \times 0.035-0.060$  in. in size, separated by Duralumin spacers 0.034 in. thick and secured by three small chromium-plated nuts and screws. Molten solder does not adhere

to these materials and the assembly may be readily dismantled after immersion.

When inserting the fluxed strips in the jig, the upper screw and spacer of the jig were removed, the fluxed portions of the tinned strips were placed face to face and the assembly was inserted between the Duralumin plates. The spacer and screw were replaced, and the jig was then ready for immersion in the solder bath. The complete jig and joint assembly is shown in part-section in Fig. 7.

*Solder Bath.*—The molten solder was contained in a welded sheet-iron bath, the inside of which had been chromium-plated to prevent "iron pick-up" by the solder. The dimensions of the bath were  $4 \times 2 \times 2$  in. deep, and the weight of solder contained was such as to make the fall of temperature on immersion of the joint-making assembly not more than  $5^{\circ}$  C.

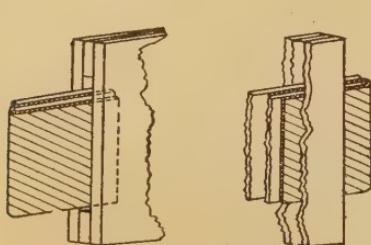


FIG. 7.—Complete Jig and Joint Assembly.

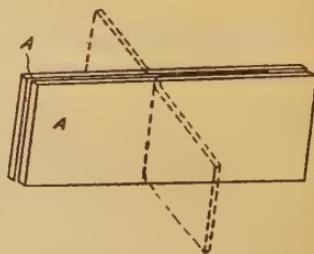


FIG. 8.—Joint as removed from Jig.

*Making the Joint.*—The solder was heated to a temperature of  $52-53^{\circ}$  C. above the liquidus, and the jig assembly was immersed completely for 20 sec. The jig was then withdrawn and held in the tongs until the solder had solidified before being placed on the bench to cool. When cool, the upper screw and spacer were removed, the jointed strips taken out of the jig and the aluminium foil unfolded.

*Determination of Joint Strength.*—The appearance of the joint as taken from the jig is shown in Fig. 8. The longer unjoined portions *A* of the two members were bent at right angles to the plane of the joint, and the members pulled apart in a testing machine, as shown in Fig. 9.

The load was applied to the joint gradually (approximately 40 lb. per min.) until the joint commenced to tear. A typical relationship between load and extension is shown in Fig. 10; when tearing commenced the variation in strength along the joint was usually  $\frac{1}{2}-1\frac{1}{2}$  lb., and if it was more than 2 lb. the joint was considered unsatisfactory and the results were ignored. The minimum load necessary to maintain tearing of the joint at the standard rate of testing was taken as the joint strength (pounds per inch).

*Appearance of Joint.*—Failure of the joint occurred at or near

the surface of the steel, so that the bulk of the solder remained on one member; owing to its greater stiffness, this member bent with a larger radius of curvature than the other member, as shown in Fig. 11.

*Notes on the Method.*—(1) This method of forming soldered joints avoids the meniscus of solder which is produced by Chadwick's technique,<sup>1</sup> and consequently simplifies the load-extension relationship. Care must, however, be taken to avoid the adherence of solder to the back of either of the members of the joint (especially at *B*, Fig. 9), since this has the effect of increasing the resistance of the members of the joint to bending and produces a peak in the load-extension curve.

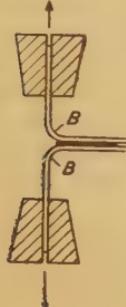


FIG. 9.—Method of Pulling the Members of the Joint.

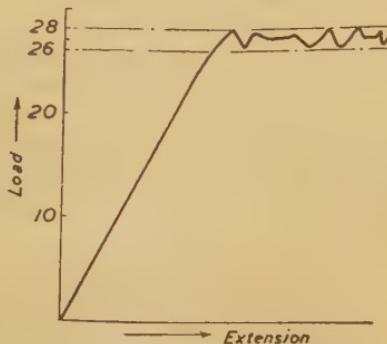


FIG. 10.—Typical Load-Extension Relationship.



FIG. 11.—Mode of Failure of Joint.

(2) With the jig described above, the accuracy and reproducibility of thickness of the solder film was found superior to that obtained when the joint members and aluminium foil were fastened together by clips, wires or springs.

(3) The apparatus is simple and inexpensive, and the operation demands very little skill when the technique has been acquired.

(4) Different thicknesses of strip may be accommodated simply by using Duralumin spacers of different thicknesses; similarly, the solder thickness may easily be adjusted by using aluminium foil of greater or lesser thickness.

*Reproducibility of Results.*—The results were found to be closely reproducible. For example, ten determinations made on hot-dipped tinplate made from cold-rolled steel strip (tested in the direction of rolling) gave the following results :

Minimum joint strength value, 45 lb. per in.  
Maximum joint strength value, 47 lb. per in.

<sup>1</sup> Chadwick, *loc. cit.*

Ten tests of samples cut from a sheet of tinplate made from pack-rolled, box-annealed sheet (tested in the direction of rolling) gave joint strengths of 29.5–32 lb. In ten tests made across the direction of rolling the joints were 3–5 lb. stronger.

*Effect of Steel Base.*—It is obvious from the nature of the test, which involves bending of the members of the joint, that the thickness and properties of the steel must exert an influence on the results obtained. Thus, the test can never be a precision determination unless these factors are kept constant. In the present investigation, all comparative work was carried out on pack-rolled sheet of similar gauge and strips for joint-strength determinations were always cut with the direction of rolling of the steel sheet in the direction of pull. As already shown, the joint strength, as determined by the method described above, is influenced by directionality in the steel base<sup>1</sup>; thus, maximum joint strength is obtained when the direction of rolling in the steel strip is at right angles to the direction of pull in the joint-strength test. Minimum values are recorded when the direction of rolling is in the direction of pulling, and the difference between the minimum and maximum values depends upon the amount of directionality in the steel base.

#### CORRESPONDENCE.

Mr. ROOSEVELT GRIFFITHS (University College of Swansea) wrote: In view of the mode of failure of the joint on testing, it would appear that a modification of the normal method of testing would be advisable. Reasoning from the facts that the two steel members of the joint are bent to different and varying angles in the test and that the stresses causing failure of the joint are rendered more complex, it would be better to bend the members to a constant value during the whole of the test.

Fig. A represents diagrammatically a suggested method. The ends of the two members are placed in suitable gripping slots in two cylinders supported in bearings, at a distance apart corresponding to the thickness of the composite joint. During the test the cylinders are rotated in opposite directions simultaneously by some such method as is merely indicated in the figure.

With this arrangement it should be possible to carry out a blank test on the steel material itself, thus taking into account, and being able to allow for, the effect of variation of its properties and thickness. This test would only require the two steel members to be

<sup>1</sup> This result confirms the findings of Dr. H. Moore and Dr. J. McKeown, of the British Non-Ferrous Metals Research Association, to whom acknowledgment is made for information supplied on methods of testing and results obtained in the course of the Association's work on solders.

placed together without any joining solder and could be carried out like the test of a soldered joint.

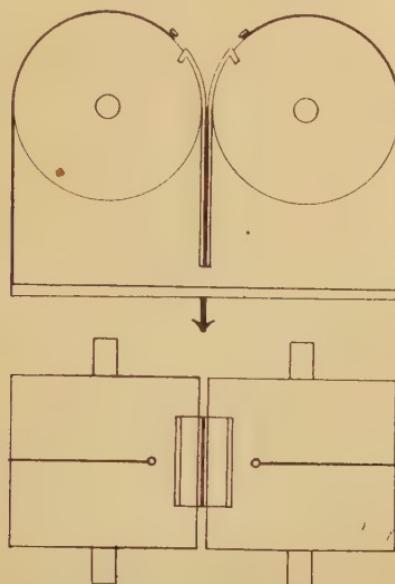


FIG. A.—Suggested Method of Testing Soldered Joints.

It would be interesting to have the authors' views on the cause or causes of the increased strength on ageing the soldered joints under the different conditions. The explanations given by Chadwick<sup>1</sup> for the ageing effect applied to somewhat different conditions of experiment.

#### AUTHORS' REPLY.

The AUTHORS wrote in reply : We thank Mr. Griffiths for his valuable suggestion for an improved method of testing; it appears to us to be sound in theory and practicable in application, but we have not, of course, had the opportunity of giving it the trial which it certainly merits.

We have given careful consideration to possible causes for the increased strength of joint found on ageing at room temperature, but we have not enough data to enable us to advance any theory with confidence. We think it not unlikely that the increase in resistance to tearing is associated with the formation or aggregation of iron-tin compound near the interface.

<sup>1</sup> R. Chadwick, *Journal of the Institute of Metals*, 1938, vol. 62, p. 277.



# THE USE OF BASIC-LINED LADLES IN THE DESULPHURISATION OF CAST IRON BY SODIUM CARBONATE.\*

BY N. L. EVANS, B.Sc., A.I.C. (RESEARCH DEPARTMENT,  
I.C.I. (ALKALI), LTD., NORTHWICH).

## SUMMARY.

A large tonnage of cast iron is desulphurised by treatment with sodium carbonate, the process normally being carried out in ladles lined with firebrick, ganister or similar siliceous refractory. These linings are attacked by soda slag, thereby impairing the efficiency of the process by contamination of the slag with silica. To meet demands for an improved degree of desulphurisation in the treatment of high-grade cast iron, the use of basic-lined ladles has been investigated. Refractories used include calcined dolomite ("Basic"), magnesia, and stabilised dolomite, all of which result in greater sulphur reduction than can be obtained in siliceous linings. The most satisfactory material used so far is "Basic," bonded with tar, which is immune to attack by soda slags and has a long life. By its use it has been possible to reduce the sulphur content of certain high-grade cast irons to 0·01% or less.

Most of the work described has been carried out on a laboratory scale in a high-frequency induction furnace, but it has been supplemented by full-scale trials.

Methods of lining ladles are described, and the technique of repairing and patching is discussed. Sufficient evidence is not yet available to determine definitely whether monolithic or brick linings are preferable, but it is felt that, on grounds of economy and long life, there is much to be said for the former. Unfired bricks made of stabilised dolomite may provide a compromise so far as cost is concerned, and they are certainly an interesting departure from normal practice.

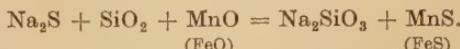
## I.—INTRODUCTION.

THE use of sodium carbonate for desulphurising cast iron has increased steadily over the past twelve years or so, until at the present time the quantity of metal treated probably exceeds two million tons per annum. The process is normally carried out without the use of any special materials for lining the ladles in which the reaction takes place. Ladles for containing molten iron are commonly lined with acid (siliceous) refractories, which may consist of sand, ganister or similar substance, rammed around a former or daubed on as a stiff paste to form a monolithic lining, or else of brickwork, usually firebrick containing 35–40% of alumina and the balance mainly silica, the joints between the bricks being a cement of composition similar to that of the bricks themselves.

It has long been known that the reaction whereby sulphur is

\* Received June 25, 1943.

removed from iron by sodium carbonate may be reversed in the presence of an excess of silica in the desulphurising slag according to the equation :



The use of sand for thickening the slag to facilitate its removal is undesirable therefore, and in its place limestone, either in the form of a powder or as dust-free chippings, is used.

Soda slag which has been used for desulphurisation usually contains upwards of 30% of  $\text{SiO}_2$ , this being derived from the ladle refractory, from furnace slag, which is often allowed to run into the ladle in spite of efforts to prevent it, and from silicon which is to some extent removed from the metal by the action of the soda slag. This degree of contamination of the slag does not matter in the case of most of the iron which is treated by sodium carbonate, and which contains before treatment 0.06–0.15% of sulphur. By the use of 1% of sodium carbonate about half this sulphur is removed, giving the metal a sufficiently low sulphur content for most industrial purposes. It is a more difficult problem, however, to effect an appreciable reduction in the sulphur content if the iron contains initially not more than 0.04% of sulphur and less than 1% of silicon. The effect of treating such an iron with even  $1\frac{1}{2}\%$  or 2% of sodium carbonate may be to reduce the sulphur by not more than 20–25%. Irons containing relatively low percentages of manganese are also difficult to desulphurise.

During the past few years a demand has arisen for a greater degree of desulphurisation of cast iron than is possible by the application of sodium carbonate in ladles with siliceous linings. The following are some of the problems which have been encountered :

- (1) In the manufacture of recarburising iron the raw material is the highest grade of hematite pig iron. This usually contains not more than 0·025% of sulphur, and it is desired to reduce this to 0·010% or less.

(2) In the production of hematite pig iron it is desirable to reduce the sulphur to the lowest possible limit, provided that the phosphorus content is also low.

(3) Owing to the war-time shortage of pig iron and, pre-war, the abundance and cheapness of steel scrap, there is a strong inducement to use up to 95% of steel scrap in the cupola charges to produce metal for electric steel furnaces, for Tropenas steel castings and for refined pig iron.

(4) In order to conserve certain alloying elements such as nickel, chromium and molybdenum, the "Rowden" process has been revived during war-time. This process involves the production, in a basic open-hearth furnace, of a synthetic pig iron from alloy-steel scrap, and it is desired to desulphurise this in the ladle after tapping it from the furnace to bring the sulphur below 0·02%.

(5) In the production of low-silicon basic iron for steel-making it is now becoming necessary to use iron ores containing more sulphur than was usual in the past. Owing to the better-grade ores having been used up, this difficulty is likely to be accentuated in the future. It is often necessary to remove more than 50% of the sulphur from the iron by a single sodium-carbonate treatment, particularly when the "acid burden" process is used.

One possible method of improving the efficiency of the sodium-carbonate process to solve the above problems is to substitute basic for acid materials in the refractory linings of the ladles used, so eliminating one source of silica in the desulphurising slag.

This is not an entirely novel suggestion, though the author is not aware that it has previously been extensively practised in Great Britain. In Luxemburg,<sup>(1)</sup> before the outbreak of war, ladles lined with tar/dolomite were used for the desulphurisation of basic Bessemer iron with sodium carbonate, and it is reported that the lives of the linings ranged from 800 to 1000 heats, as compared with 400 to 600 heats in the case of firebrick linings. When not in use, these linings were kept hot over a blast-furnace-gas burner. At a German works,<sup>(1)</sup> where sodium carbonate for desulphurisation was pre-melted, a rotary furnace lined with tar-bonded dolomite was used for this purpose. After treatment, the iron and soda slag were separated from one another by pouring them into a syphon ladle, this also being lined with tar-bonded dolomite. At another German works<sup>(2)</sup> experiments were made with pig iron ladles lined with rammed dolomite, rammed magnesite, and rammed dolomite with 10% of graphite added. The blast-furnace runner was also lined with dolomite, though this is stated to have caused some trouble on account of cracking. The percentage of sodium carbonate used is not stated, but desulphurisation was increased from 32.7% in a fireclay lining to 48.2% in a basic lining.

The present paper describes experiments which have been carried out during the past three years to find in greater detail how the use of basic linings affects the sodium-carbonate process.

## II.—AVAILABLE BASIC LADLE-LINING MATERIALS.

### (a) *Magnesite.*

This is usually employed in the form of bricks, but monolithic linings can be made from the ground refractory bonded with magnesium chloride solution and 5 or 6% of light sodium carbonate. Magnesite was used in a few experiments in the present investigation, but in view of the fact that it is in short supply in war-time its use was not considered very seriously; but it may be said that desulphurisation in magnesite linings is about equal to that in dolomite, other conditions being constant.

(b) *Calcined Dolomite ("Basic").*

Dolomite is found in various parts of Great Britain and supplies are reasonably plentiful. It consists of calcium-magnesium carbonate, and before it can be used as a refractory it must be burnt at a temperature of about 1800° C. to drive off all CO<sub>2</sub>. Unfortunately, it is not stable in this condition, and if exposed to the atmosphere at normal temperatures it hydrates (slakes) and disintegrates to a powder. Its use is, therefore, confined mainly to the linings of steel furnaces which are kept hot continuously. It is graded, and bonded by mixing it with about 6% of dehydrated tar.

(c) *Stabilised Dolomite.*

"Basic" can be stabilised against hydration either temporarily or permanently. Temporarily this may be effected by mixing stearic acid (0·016%) with the Basic. This renders the material waterproof, so that it can be transported, and kept in stock for reasonable periods without deteriorating. Mixing with 4% of dehydrated tar gives a similar degree of protection. Such temporary methods are of some value for treating Basic which is to be used in, say, an open-hearth furnace and kept hot continuously.

Permanent stability is imparted to Basic by combining silica with it, to form tricalcium silicate and magnesia, leaving no free lime. The stabilised refractory contains 15–17% of silica and is prepared by grinding dolomite and serpentine with water, forming a slurry which is fed into a rotary kiln and fired at a temperature exceeding 1600° C.<sup>(3)</sup> It may be used in the form of clinker as it comes from the kiln, or it may be crushed and ground, and moulded into shape after mixing it with about 6% of water. The shapes may be used in the green state after drying, or may be refired before use. Other materials such as metallic oxides may be incorporated as fluxes, and bentonite may be added to give plasticity to the material when mixed with water.

(d) *Serpentine.*

Serpentine is a mineral of which large deposits are available in Britain. It consists of magnesium orthosilicate.

### III.—EXPERIMENTAL WORK.

The experimental work which has been carried out is divided into two parts: (1) Small-scale work in the laboratory; (2) full-scale work in foundries and in iron and steel works.

(a) *Laboratory Work.*

This was carried out in a Metropolitan-Vickers high-frequency induction furnace and was concerned with trying out the action of soda slags on various refractory materials and finding how the use of different refractories affects the degree of desulphurisation of certain types of cast iron.

Sillimanite crucibles (Morgan Crucible Co., Ltd., ΔV.5) are normally used in the induction furnace. Sillimanite is aluminium silicate ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  containing 63% by weight of  $\text{Al}_2\text{O}_3$ ) and offers fairly good resistance to attack by sodium-carbonate slag. Ladle linings are usually made of either firebrick, loam or sand, all of which are attacked by sodium-carbonate slag to varying degrees. Sand and loam are more friable than any sort of fired brick or crucible, and therefore tend to contaminate the soda slag with silica to a greater extent until they have become cemented by slag.

Sillimanite crucibles are lined with other refractory materials in the following manner: The liming material is brought to the required condition by the addition of a binder and is then rammed into the crucible round a tapered wooden former, to give a lining  $\frac{1}{2}$  in. thick (Fig. 1). The tool used for ramming has one end tapered for ramming the sides and to prevent layering of the material, and the other end flat for consolidating the bottom and finishing the top edge. A  $\frac{1}{2}$ -in. thick lining reduces the capacity of a crucible from 11–12 lb. to  $6\frac{1}{2}$ –7 lb. of cast iron.

The following bonding materials were used :

(a) *Dehydrated tar*, used with Basic. It must be completely burned-off in a gas-fired furnace at about  $750$ – $850^\circ$  C. before the lined crucible is used in the induction furnace; otherwise it penetrates the crucible walls and condenses in the zircon sand which surrounds the coil, upsetting the working of the furnace.

(b) *Magnesium chloride* (5% aqueous solution), used with magnesia linings. Alone it is not sufficient, the linings being too friable. A satisfactory lining was produced with the following mixture :

Old ground magnesia brick	.	.	.	658.3 g.
Light $\text{MgO}$	.	.	.	109.7 g.
Light $\text{Na}_2\text{CO}_3$	.	.	.	38.4 g.
Magnesium chloride (as 5% solution)	:	.	.	20.0 g.

(c) *Sodium silicate*, used as a bond for sand or stabilised dolomite. A grade of silicate solution having a  $\text{SiO}_2 : \text{Na}_2\text{O}$

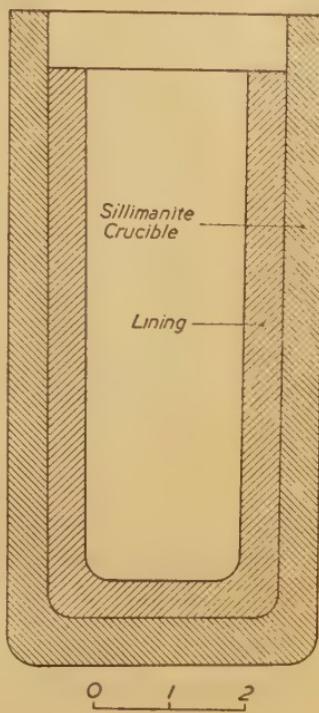


FIG. 1.—Lined Crucible for Induction Furnace.

ratio of about 2 : 1 and a specific gravity of about 1·5 is suitable. It requires dilution with water before use.

(d) Water, used with sand and stabilised dolomite.

Rammed linings are porous and the first time they are used for desulphurisation with sodium carbonate the soda slag is usually almost completely absorbed in the lining and does not remain in contact with the melt sufficiently long. For this reason first melts do not always give representative results. This impregnation with slag strengthens the lining, however, and supports the view that sodium carbonate or ground soda slag might be mixed with certain refractories to act as a bond.

(b) *Results of Desulphurising Experiments.*

Some preliminary trials were carried out on the desulphurisation of a common grey iron of the following composition :

Total Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
3·43%	1·66%	0·102%	1·49%	0·67%

On treating this iron with sodium carbonate, the results contained in Table I. were obtained.

TABLE I.—*Common Grey Iron. Desulphurisation with Sodium Carbonate.*

Melt No.	Refractory.	Sodium Carbonate Used. %.	Sulphur Content After Treatment. %.	Percentage of Sulphur Removed.
M1200 *	Sillimanite	1	0·051	50·0
M1201	"	2	0·039	61·8
M1175 *	Dolomite	1	0·039	61·8
M1191 *	"	1	0·036	64·7
M1192	"	1	0·036	64·7
M1194 *	"	1	0·031	69·6
M1195	"	1	0·034	66·6
M1196	"	1	0·029	71·5
M1197	"	2	0·031	69·6
M1218 *	Magnesia	1	0·093	8·8
M1219	"	2	0·039	61·8

\* This mark, in this and later Tables, indicates a first melt in a refractory. Owing to the porosity of rammed linings the soda slag is liable to be rapidly absorbed in the first melt and the desulphurisation of the metal may not be as efficient as in subsequent melts after the pores are sealed.

An attempt was also made to simulate the composition of the synthetic pig made in a basic steel furnace by melting and carburising alloy-steel scrap (the Rowden process). A mixture was made up containing the following :

American washed iron	.	.	.	.	4 lb. 3 oz.
Mild steel	.	.	.	.	2 lb. 1 oz.
Ferro-silicon (70%)	:	:	:	:	$\frac{1}{4}$ oz.
Manganese	.	.	.	.	1 oz.

Melts were also made of mild steel, and these were carburised with either anthracite or wood charcoal before the sodium-carbonate treatment was applied. The desulphurisation results are recorded in Table II.

Following the preliminary trials, several series of melts were made with different irons, in both sand and tar/dolomite linings, with sodium-carbonate additions varying from  $\frac{1}{2}\%$  to  $2\frac{1}{2}\%$ .

TABLE II.—*American Washed Iron and Carburised Mild Steel. Desulphurisation with Sodium Carbonate*

Melt No.	Material.	Refractory.	Sodium Carbonate Used. %.	Sulphur Content. %.		Percentage of Sulphur Removed.
				Before.	After.	
M1176	American washed iron	Dolomite	2	0.034	0.025	26.5
M1198	mixture.	,,	1	0.034	0.020	41.2
M1199*			2	0.037	0.021	43.2
M1202	Carburised mild steel (anthracite).	Sillimanite	2	0.098	0.036	63.4
M1213*	Carburised mild steel (charcoal).	Dolomite	1	0.041	0.035	14.7

\* First melt, see footnote to Table I.

(1) *Common Grey Iron*.—The analysis of this material before remelting was :

Total Carbon.	Silicon.	Sulphur.	Phosphorus	Manganese.
3.34%	1.75%	0.152%	1.17%	0.60%

The results of desulphurisation tests will be found in Table III.

TABLE III.—*Common Grey Iron. Desulphurisation with Sodium Carbonate in Dolomite and in Sand Linings*.

Sodium Carbonate. %.	Dolomite Lining.			Sand Lining.		
	Melt No.	Sulphur.		Melt No.	Sulphur.	
		After Treatment. %.	Per-cent age Removed.		After Treatment. %.	Per-cent age Removed.
$\frac{1}{2}$	M1239 *	0.075	50.6	M1231 *	0.114	25.0
$\frac{1}{2}$	M1285	0.065	57.2			
1	M1240	0.079	48.0	M1232	0.098	35.5
$1\frac{1}{2}$	M1241 *	0.061	59.8	M1233	0.090	40.8
$1\frac{1}{2}$	M1284	0.038	75.0			
2	M1242	0.056	63.2	M1234	0.073	52.0
$2\frac{1}{2}$	M1243	0.067	55.9	M1235	0.062	59.2
$2\frac{1}{2}$	M1283	0.037	75.7			

\* First melt, see footnote to Table I.

(2) *Grey Hematite Iron.*—The analysis of this material before remelting was :

Total Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
4.41%	1.49%	0.035%	0.023%	0.76%

The desulphurisation test results are collected in Table IV.

TABLE IV.—*Grey Hematite Iron. Desulphurisation with Sodium Carbonate in Dolomite and Sand Linings.*

Sodium Carbonate. %.	Dolomite Lining.			Sand Lining.		
	Melt No.	Sulphur.		Melt No.	Sulphur.	
		After Treatment. %.	Per- centage Removed.		After Treatment. %.	Per- centage Removed.
½	M1263	0.024	31.5	M1268	0.033	5.8
1	M1262	0.0205	41.4	M1267	0.027	22.8
1½	M1261	0.0192	45.2	M1266	0.027	22.8
2	M1260	0.018	48.6	M1265	0.020	42.9
2	M1288 *	0.0175	50.0	M1264 *	0.025	28.6
2½	M1259 *	0.0175	50.0			
2½	M1289	0.014	60.0			

\* First melt, see footnote to Table I.

(3) *Miscellaneous Materials and Reagents.*—References have

appeared in recent technical literature<sup>(4, 5)</sup> to the desulphurisation of cast iron by mixtures of sodium carbonate and limestone added to the metal either in the molten condition or as sintered mixtures. Oelsen used the double carbonate, containing 48.5% of  $\text{CaCO}_3$  and 51.5% of  $\text{Na}_2\text{CO}_3$  by weight, and having a melting point of  $813^\circ\text{C}$ . It was thought that it might be opportune to try similar mixtures in acid and basic linings. The results are interesting, though the series of tests was discontinued when it was seen that the mixtures have no definite advantage over sodium carbonate used alone. The diagram (Fig. 2) of the system  $\text{Na}_2\text{CO}_3-\text{CaCO}_3$  ac-

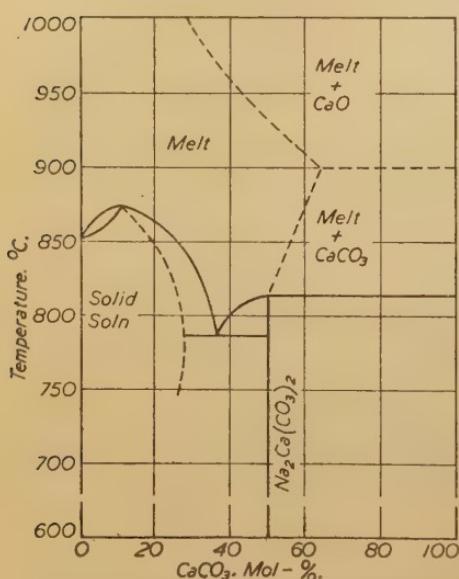


FIG. 2.—The  $\text{Na}_2\text{CO}_3-\text{CaCO}_3$  System (Niggli<sup>(6)</sup>).

cording to Niggli<sup>(6)</sup> shows that, in addition to the double carbonate, there is a eutectic, having a melting point of 786° C.

Small quantities of both the eutectic and the double carbonate were prepared by mixing together light sodium carbonate and light calcium carbonate, sintering the mixtures for about 1 hr. at 715–720° C., cooling in a desiccator and grinding. Test results showed that the mixtures do not appear to have any advantages as compared with sodium carbonate alone, but they confirmed the advantage of using basic linings.

The mixed carbonates melt when first added to the molten iron, but after a few seconds they solidify and form a dry clinker.

It was suggested to the author that cast iron might be dephosphorised by treatment with mill scale mixed with the desulphurising reagent. This and other suggested methods of dephosphorising cast iron were tried, without success. Attempts were made to desulphurise steel and these showed slight promise.

A further suggestion made to the author during the course of the investigation was that serpentine (magnesium orthosilicate) might function as a basic refractory. It was tried, but the results were disappointing, and the crucible linings were severely attacked on the slag-line.

The desulphurisation of iron in stabilised dolomite was studied in a large number of melts, as this refractory has advantages over Basic for lining ladles which are allowed to cool down and remain for long periods in atmospheres sufficiently humid to cause the disintegration of the Basic. As would be expected from the presence of 15% of silica in stabilised dolomite, the results, so far as desulphurisation is concerned, were not as good as those obtained in tar/dolomite linings. They were better, however, than results in siliceous linings, and the practical advantages of the stabilised product should not be lost sight of, such as, for example, the ease with which it can be stocked, or supplied to foundries in small quantities.

The results of all the miscellaneous tests are set out in Tables V. and VI.

#### (c) *Final Series of Laboratory Tests.*

After the experience gained in the experiments already described, a series of melts was planned under conditions as nearly constant as possible, to compare the action of sodium carbonate on various types of cast iron in the four available refractory linings. The refractories used were :

- Calcined dolomite, tar-bonded.
- Stabilised dolomite, water-bonded.
- Serpentine, water-bonded.
- Loam, water-bonded.

TABLE V.—Miscellaneous Materials and Reagents. Desulphurisation Tests.

Material.	Reagent.	Dolomite Lining.				Sand Lining.			
		Melt No.	Sulphur. %.		Percent- age of Sulphur Removed.	Melt No.	Sulphur. %.		Percent- age of Sulphur Removed.
			Before.	After.			Before.	After.	
Grey hematite iron	Sodium carbonate, 1% 2% Sintered mixture, equal parts $\text{Na}_2\text{CO}_3$ and $\text{CaCO}_3$ , 2%	M1207 *	0.012	0.008	33.3				
		M1208	0.012	0.008	33.3				
		M1214 *	0.024	0.016	33.3				
White hematite iron	Sodium carbonate, 1% 2% Sodium carbonates, 1% Mill scale, Sodium carbonate, 1% Mill scale, Limestone,	M1221 *	0.013	0.010	23.1				
		M1222	0.013	0.006	53.8				
		M1223	0.013	0.010	23.1				
		M1224	0.013	0.008	38.6				
Common grey iron	Double carbonate of sodium and calcium, 1% 2% 2% Eutectic of sodium carbonate and lime- stone, 2%	M1244	0.162	0.072	52.6	M1236 *	0.152	0.124	18.4
		M1245	0.152	0.098	35.5	M1237	0.152	0.106	30.2
		M1290	0.152	0.054	64.4				
		M1246	0.162	0.086	43.4	M1238	0.152	0.113	25.6

\* First melt, see footnote to Table I.

TABLE VI.—Miscellaneous Materials and Reagents. Desulphurisation and Dephosphorisation Tests.

Material.	Reagent.	Melt No.	Sulphur, %. Before.	Sulphur, %. After.	Percent- age of Sulphur Removed.	Linings and Remarks.
White hematite pig iron + 1% of silicon	Sodium carbonate, 21% 21% 21% 21% 20% 20% 20% 20% 20% 20% 20% 20% 20% 20% 20% 20% 20%	M1324 * M1325 M1326 M1329 * M1330 M1331 M1332	0·013 0·013 0·013 0·013 0·013 0·013 0·013	0·013 0·012 0·011 0·014 0·012 0·010 0·010	Nil 7·7 16·4 Nil 7·7 23 23	Stabilised dolomite bonded with 2% of sodium silicate powder and 5% of water. Same as for M1324. New lining, as above. Same as for M1329. Same as for M1329-30. Same as for M1329-31.
White hematite pig iron	Sodium carbonate, 2% 20% 20%	M1455 * M1456 M1457	0·013 0·013 0·035	0·012 0·012 0·012	7·7 7·7 6·6	Stabilised dolomite bonded with 3% of water and 2% of sodium silicate solution. Same as for M1455. Same as for M1455-56.
Grey hematite pig iron	Sodium carbonate, 25% { Limestone, 75%}	M1392 * M1393 * M1415 * M1418 *	0·072 0·046 0·028 0·028	0·051 0·045 0·030 0·036	29 2·2 Nil Nil	Stabilised dolomite. Magnesite. Magnesite. Magnesite.
Mild steel 0·73% carbon steel	Sodium monoxide, 75% Calcium hydroxide, 25% } Bleaching powder Fluorspar, Sodium monoxide, 3% }	M1422 * M1423 M1425 * M1428 *	0·152 0·152 0·152 0·152	0·055 0·128 ... 0·023	63·8 15·8 ... 85	Attempts to Dephosphorise Iron. Phosphorus. Before. After. Magnesite . . . 1·17% Magnesite . . . 1·17% Stabilised dolomite . . 1·17% Stabilised dolomite . . 1·17% Stabilised dolomite . . 1·11% Same as for M1431.
Common grey iron	Sodium monoxide, 20% Bleaching powder, 7 parts Fluorspar, Sodium monoxide, 3% }	M1431 v M1432	0·035 0·013	0·012 0·010	66 23	Serpentine Linings. Serpentine bonded with 3% of water. Not a strong lining. Serpentine bonded with 3% of water and 2% of sodium silicate solution. Good strength. Same as for M1452. Same as for M1452-53.
Grey hematite pig iron White hematite pig iron	Sodium carbonate, 20% 2% 20% 20%	M1451 v M1452 e M1453 M1454	0·035 0·013 0·013 0·035	0·030 0·018 0·011 0·020	14 Nil 16 1/4 4; 1/2	* First melt, see footnote to Table I.

In each lining, four melts were made in the following order, treating each melt with approximately 2% of granular sodium carbonate :

- Melt 1—Grey hematite pig iron.
- „ 2—Grey hematite pig iron.
- „ 3—White hematite pig iron.
- „ 4—Common grey iron.

The reason for making two melts of grey hematite iron was that, as previously explained, in the first melt in a rammed lining the soda slag is almost entirely absorbed by the lining unless the dosage of sodium carbonate is fairly high. The first melt in the series now to be described was, therefore, primarily to seal the pores of the refractory.

The analysis of the grey hematite iron as received was :

Total Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
3.86%	2.57%	0.019%	0.035%	0.87%

The analysis of the white hematite iron as received was :

Total Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
3.12%	0.14%	0.029%	0.032%	0.18%

The analysis of the common grey iron is given above in Section III. (b) (1).

The results of this series of tests are given in Table VII. They show that :

(1) In the various refractory materials tested, the efficiency of desulphurisation with sodium carbonate is in the following order :

- Calcined-dolomite/tar.
- Stabilised dolomite.
- Serpentine.
- Loam (sand).

(2) Sodium carbonate gives a worth-while degree of desulphurisation in both calcined-dolomite/tar and stabilised dolomite, even when the initial sulphur content of the iron is low (0.03% or less). With such irons, very little desulphurisation takes place in serpentine or sand linings.

(3) An appreciable degree of desulphurisation takes place in all the types of lining tested when the initial sulphur content of the iron is of the order of 0.1-0.2%.

*Note.*—The results set out in Table VII. are comparative among themselves, but should not be regarded as indicative of the actual desulphurisation to be expected under full-scale working conditions. In the induction-furnace experiments the reagent is put on top of the melt, whereas in full-scale working the reagent is put in the bottom of the ladle and the metal is tapped on to it. It should also

TABLE VII.—*Results of Desulphurisation with 2% of Sodium Carbonate in Four Different Refractory Linings.*

Lining Material :	Calcined Dolomite/Tar.		Stabilised Dolomite.	Ser- pentine.	Loam (Sand).
<i>Grey Hematite Pig Iron.</i>					
Sulphur, % : Before . . .	0.019	0.019	0.019	0.019	0.019
After . . .	0.008	0.012	0.013	0.020	0.021
Percentage of sulphur re- moved . . .	58	36.8	31.5	Nil	Nil
Silicon, % : Before . . .	2.57	2.57	2.57	2.57	2.57
After . . .	1.96	1.95	1.98	2.11	2.30
Percentage of silicon re- moved . . .	23.7	24.1	23	17.9	10.5
<i>Grey Hematite Pig Iron.</i>					
Sulphur, % : Before . . .	0.019	0.019	0.019	0.019	0.019
After . . .	0.008	0.012	0.015	0.015	0.018
Percentage of sulphur re- moved . . .	58	36.8	21	5.3	5.3
Silicon, % : Before . . .	2.57	2.57	2.57	2.57	2.57
After . . .	2.11	2.04	2.26	2.30	2.30
Percentage of silicon re- moved . . .	17.9	20.6	12	10.5	10.5
<i>White Hematite Pig Iron.</i>					
Sulphur, % : Before . . .	...	0.029	0.029	0.029	0.029
After . . .	...	0.009	0.014	0.014	0.024
Percentage of sulphur re- moved . . .	...	69	51.8	17.2	17.2
Silicon, % : Before . . .	...	0.14	0.14	0.14	0.14
After . . .	...	0.06	0.06	0.10	0.10
Percentage of silicon re- moved . . .	...	57	57	28.5	28.5
<i>Common Grey Iron.</i>					
Sulphur, % : Before . . .	0.152	0.152	0.152	0.152	0.152
After . . .	0.032	0.059	0.083	0.078	0.078
Percentage of sulphur re- moved . . .	79	61	45.4	48.6	48.6
Silicon, % : Before . . .	1.75	1.75	1.75	1.75	1.75
After . . .	1.14	1.10	1.15	1.21	1.21
Percentage of silicon re- moved . . .	34.8	37.1	34.2	30.8	30.8

be pointed out that it is not easy to maintain constant temperature conditions in a small induction furnace and this may account for some of the slight discrepancies in the work. In full-scale working it should be possible to maintain a much more constant temperature from melt to melt.

#### (d) Desiliconisation of Cast Iron.

Treatment by sodium carbonate invariably removes silicon from cast iron, and with an acid ladle lining material it is usual for the

silicon content to be reduced by about 0·1–0·2%, e.g., from 2·0% to 1·85%, under full-scale working conditions.

The analysis of sodium-carbonate slags usually shows the presence of 25–35% of silica. It would be expected that most of this would come from the ladle lining and that it would be lower when a basic lining was used. This is, in fact, the case, but the silica content of the slags remains surprisingly high, in the region of 20–25%. The results given in Table VII. show that the loss of silicon from the melt is higher in a basic than in a siliceous lining. This is confirmed by some of the preliminary experiments, the silicon losses being set out in Table VIII.

TABLE VIII.—Desiliconisation by Sodium Carbonate in Dolomite and Sand Linings.

Sodium Carbonate Used (Approx.):	Desiliconisation, %.			
	1%.	1%.	1½%.	2%.
<i>Common Grey Iron (1·6% Silicon).</i>				
In dolomite lining . . . .	0·22	0·32	0·35	0·40
In sand lining . . . .	0·07	0·19	0·32	0·28
<i>White Hematite Pig Iron (0·57% Silicon).</i>				
In dolomite lining . . . .	0·05	0·10	0·16	0·23
In sand lining . . . .	0·07	0·11	0·08	0·14
<i>Grey Hematite Pig Iron (1·4% Silicon).</i>				
In dolomite lining . . . .	0·11	0·16	0·24	0·29
In sand lining . . . .	0·10	0·21	0·20	0·29

The differences are, in most cases, not sufficiently pronounced to indicate more than a tendency for the metal in basic linings to lose more silicon, but the tendency is in the direction which would be expected and may be of importance in the treatment of basic iron.

#### (e) *Visible Attack on the Refractories.*

After the series of experiments set out in Table VII., the dolomite/tar and stabilised-dolomite linings showed practically no signs of attack by the soda slags. The surface was glazed, but the soda slag did not appear to have penetrated to any considerable depth.

Both the serpentine and the loam linings were severely attacked and were cut by very deep slag-lines.

#### IV.—METHODS OF PREPARING BASIC LININGS FOR LADLES.

Ladle linings may be prepared by ramming the ground refractory, mixed with a suitable binder, round a wooden or metal

former to produce a monolithic lining, or they may be constructed of refractory bricks.

Basic, on account of its strong tendency to hydrate, must be bonded with tar and not with water.

The Basic is prepared by grinding to produce a mixture of particle sizes with a high packing density, and is mixed in a light pan-mill with dehydrated tar preheated to 80° C. About 6% of tar by weight is usually used. The tar/dolomite mixture is reheated to about 70° C., and is rammed with pneumatic rammers. The former for shaping the lining is best made of wood covered with sheet steel and oiled before use. In preparing the ladle bottom, particularly in the case of large ladles into which molten iron is to be poured from a considerable height, it is desirable to have one or more layers of brick underneath the dolomite. Ordinary fire-brick may be used and it also acts as a heat insulator. It is usual for the tar to be burned-out before the ladle is used, but this is not always done.

In lining small ladles (up to 2 tons) it is not necessary to have any brick backing for the sides. The tar/dolomite mixture can be rammed directly on to the shell of the ladle.

It has been found that, once a dolomite lining has received a coating of slag, it does not disintegrate rapidly, and it is possible, for example, to let it get cold for repairs at the week-end without any visible disintegration taking place.

When stabilised dolomite clinker or parging cement is used the technique is similar, but the refractory can be bonded with 6½% of water in place of dehydrated tar, as it has cementing properties. The following method was used in lining 2-ton ladles at the works of Messrs. Kryn and Lahy (1928), Ltd., of Letchworth. The bottom of the ladle was first levelled with 2-3 in. of refractory mixed with the requisite quantity of water. This layer was rammed hard and was then covered with a 3-in. layer of stabilised-dolomite bricks jointed with some of the ground mixture. Another 3-in. layer of the latter was rammed on top of the bricks to complete the bottom. The cast-iron former was then placed in position and the sides of the ladle were rammed. The lining was then air-dried for 24 hr., followed by 24 hr. with a wood fire in the ladle, then 24 hr. with a coke fire; finally, it was heated over-night inverted over a coke fire with forced draught.

A small quantity of sodium silicate may be dissolved in the water used for mixing stabilised dolomite to increase the strength of the bond. It is not desirable to use more silicate than is absolutely necessary, as it will reduce the refractoriness of the mixture. A suitable grade of sodium silicate for the purpose is a solution having a SiO<sub>2</sub>:NaO<sub>2</sub> ratio of approximately 2 : 1 and a specific gravity of approximately 1.5; 2% of this diluted with about twice its volume of water and mixed with the refractory gives satisfactory results.

## V.—FULL-SCALE EXPERIMENTS.

Several full-scale experiments have been carried out, or are still in progress, by firms using the sodium-carbonate process for desulphurising molten iron. Much useful information has been accumulated, demonstrating the advantage of basic-lined ladles for this process due to the absence of chemical attack on the lining by soda slags and the improved degree of desulphurisation.

(a) *Stabilised Dolomite, Tar-Bonded.*

In the early stages of the investigation two ladles were lined with tar/stabilised-dolomite. In both cases the results were inconclusive, but appeared on the whole to be better than those of parallel tests in acid linings. The linings themselves gave a certain amount of trouble. The grading of the dolomite clinker was too coarse, and it was not possible to get the upper part of the linings properly consolidated, nor were the linings fired at a sufficiently high temperature to produce a good bond.

(b) *Stabilised Dolomite, Water-Bonded.*

Stabilised dolomite can be bonded with water or tar, and experiments with the former were carried out by Messrs. Kryn and Lahy (1928), Ltd. The details of the method used for lining the ladle are recorded above in Section IV.

The ganister-lined ladles normally used are always severely attacked near the bottom by soda slag. The reason for this is that the ladles, which are used for the desulphurisation of cupola iron and its transfer to Tropenas converters, always carry an excess of metal. Consequently, after the converter has been filled a shallow pool of molten iron remains in the ladle, and the dose of sodium carbonate for the next charge of metal is put in in readiness. The sodium carbonate melts and attacks the ladle lining at a level of 1–4 in. from the bottom, forming a deep undercut. If, as occasionally happens, the residual metal solidifies, it cannot be removed without

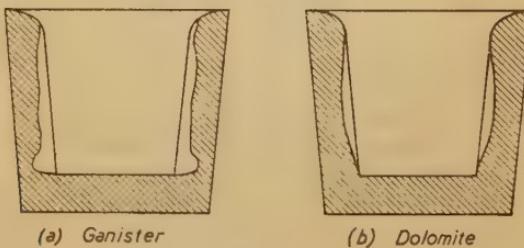


FIG. 3.—Wear of Ladle Linings (diagrammatic).

further serious damage to the lining (see Fig. 3 (a)). Patching is necessary after only a short period of use.

The first ladle lined with stabilised dolomite behaved much better. There was no apparent wear for three days and no patching was needed until after the fourth day. No undercutting took place, but the lining became barrel-shaped, which would appear to be due to attrition by the metal and not to attack by soda slag (*see Fig. 3 (b)*).

This lining resulted in better desulphurisation than is obtained with ganister linings. The average sulphur content of the metal after treatment was 0·037%, as compared with 0·043% in ganister linings.

After four days' use, the lining was patched with a specially prepared stabilised-dolomite cement mixed with  $11\frac{1}{2}\%$  of water. This patching material began to come away from the lining after three or four heats of metal had been through it. In the author's opinion, this unsatisfactory behaviour of the patching material was due to the failure to chip away the glaze from the lining before patching it. Undercutting of the old lining by means of a suitable tool would also assist the adhesion of the patches.

#### (c) *Unfired Stabilised-Dolomite Bricks.*

One of the disadvantages of some types of basic bricks is their tendency to spall much more readily than siliceous refractories do. Therefore, when it was decided to try a stabilised-dolomite-brick-lined ladle at Messrs. Kryn and Lahy (1928), Ltd., the suggestion was made to try unfired bricks, as it was thought that their resistance to spalling might be better than that of the ordinary fired bricks. A subsequent spalling test showed failure after four reversals (heating and cooling), as compared with two reversals in the case of the fired bricks. The unfired bricks were fragile, and a number were broken in transit, but since these experiments were carried out the makers have succeeded in improving the bond considerably.

The ladle lining consisted of a  $4\frac{1}{2}$ -in. thickness of brick, with a backing of 2 in. of parging cement. It behaved well for 100 heats of metal, all treated with sodium carbonate. After this period it appeared to justify further patching. The degree of desulphurisation was similar to that in a rammed stabilised-dolomite lining.

#### (d) *Stabilised-Dolomite Bricks.*

Messrs. Kryn and Lahy (1928), Ltd., have experimented with a ladle lined with stabilised-dolomite bricks. Unfortunately, on account of war conditions, it was not possible to make these bricks in special shapes, only "squares" and "splits" being available. This resulted in some of the joints being thicker than is desirable, but in spite of this the lining behaved extremely well. The jointing material was a cement with a stabilised-dolomite base, and this resisted sodium-carbonate slag satisfactorily. Patching was carried out when necessary with the same material, and daily renewal was

needed once it had been started. (A special patching material—also with a stabilised-dolomite base—is now available, and should be used in preference). It is probable that it would have lasted longer had it been keyed-in by first undercutting the original lining and removing the surface glaze. Spalling gave practically no trouble at all. On the first day that the lining was in use it appeared to be spalling a little, but this did not continue once the bricks had become impregnated with soda slag.

The average sulphur content of the finished steel was 0·032%, as compared with 0·043% when a ganister-lined ladle is used.

(e) *Semi-stabilised Dolomite Bricks.*

Semi-stabilised dolomite bricks are produced for use in positions not exposed to hydration. They are given a temporary stability sufficient to protect them for about a month before they go into service. The author has not had an opportunity of testing such bricks in a ladle lining, but some of them have been kept in contact with molten sodium carbonate at a maximum temperature of 1020° C. for some days. They resisted chemical attack very well, and only slight signs of cracking were observed, whereas the fully stabilised bricks cracked much more.

## VI.—CONCLUSIONS.

It has been shown that the use of basic-lined ladles for carrying out the sodium-carbonate process for desulphurising cast iron results in an appreciably greater degree of desulphurisation than is obtained under otherwise similar conditions in siliceous refractory linings. The improvement is most marked in the treatment of cast iron having initially a sulphur content less than 0·04%. Such iron is sometimes difficult to desulphurise to an appreciable extent in siliceous-lined ladles, but in basic linings it has, in some cases, been possible to reduce the sulphur content to a figure below 0·01%.

Suitable basic lining materials are magnesite, dolomite and stabilised dolomite. The first of these being in short supply, attention was directed mainly to the other two. The best results were obtained in linings of tar-bonded dolomite. Stabilised dolomite, containing about 15% of silica, is not quite so good, but it gives results superior to those obtainable in firebrick, loam or other acid linings, and it has the advantage over unstabilised dolomite that it can be kept in stock without deterioration by users who have no proper facilities for mixing tar and dolomite and require only small quantities of lining material at a time.

The technique of preparing monolithic basic linings appears to be fairly straightforward. There is scope for further investigation on the subject of basic-brick linings. The question of spalling appears to be less serious in the presence of sodium carbonate slag than the results of the standard spalling test would suggest.

Methods of patching linings after a period of use are not so successful as could be desired, and it is felt that this matter would repay further investigation.

The author wishes to acknowledge the help received from a number of individuals and firms who have assisted this investigation by supplying metal and refractory samples and by carrying out full-scale trials. In particular, he would like to mention Mr. E. Shaw, of The Refractory Brick Company of England, Ltd., and the late Mr. J. Deschamps, and Mr. Derek Wells, of Messrs. Kryn and Lahy (1928), Ltd., without whose co-operation very little could have been accomplished.

#### APPENDIX.—Analyses of Refractories Used.

The analyses of the refractories used in this investigation are recorded in Table IX.

TABLE IX.—*Analyses of Refractory Materials Used in this Investigation.*

Tar/Dolomite Mixture. Analysis of Dolomite after Extraction of Tar.	Stabilised Dolomite Clinker.	Parging Cement.	Serpentine.	Stabilised-Dolomite Brick.	Unfired Stabilised Dolomite Brick.	Semi-stabilised Dolomite Brick.
CaO. % .	53.28	37.71	38.14	0.72	40.04	37.0
MgO. % .	33.76	33.61	40.20	41.46	40.30	37.5
SiO <sub>2</sub> . % .	4.05	15.57	16.34	41.16	14.44	20.0
Fe <sub>2</sub> O <sub>3</sub> . % .	1.45	...	3.27	8.98	3.44	...
Al <sub>2</sub> O <sub>3</sub> . % .	2.15	...	...	...	1.50	...

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## CORRESPONDENCE.

Mr. L. W. SANDERS (Messrs. Lake and Elliot, Ltd., Braintree, Essex) wrote : The author is to be congratulated upon his efforts to improve the effectiveness of sulphur elimination in cast iron by the sodium-carbonate process using basic-lined ladles.

At Braintree we have carried out a series of experiments with calcined dolomite, bonded with tar, for linings in ladles used for desulphurising cupola iron for the Tropenas converter process.

It is considered that the author's description of methods for preparing basic-lined ladles is inadequate and that an elaboration upon the particle size, packing density and the expansion of the material at metal temperature is necessary.

We find that the maximum life of a lining is obtained when the particle size of the monolith is no greater than  $\frac{1}{2}$  in., and if the size is increased to  $\frac{3}{4}$  in. the life of the lining is reduced by approximately 40%.

It is difficult to understand the reason for ramming the tarred dolomite at 70° C., as at this temperature it is very spongy, being difficult to consolidate, and, unless the formers are left in position until the monolith cools to a normal temperature, there is a definite tendency for the dolomite to collapse.

The addition of 6% of tar does not appear to be sufficient to produce a satisfactory bond when the dolomite is fine, and it is probable that, if maximum consolidation is to be obtained, it will be found necessary to increase the bond to approximately 10%.

We also found that it is not good policy for the ramming to be extremely severe (that is, taken to the maximum hardness); it should only be enough to consolidate the lining, as the expansion of the material is such that, when ramming is taken to the maximum density, there is insufficient space between the grains for expansion to take place, and the material takes the line of least resistance, pushes outwards and breaks down. This view is supported by the behaviour of the bottoms of ladles which were rammed in layers of 1 in. to a depth of 7 in. After 4 heats of metal had been passed through, the bottom began to peel off in layers, exactly as they were rammed. At the end of the week a new bottom was rammed, the dolomite being of fairly large grain size, and was consolidated in bulk. After 60 heats no peeling had occurred.

Regarding the wear of basic linings, we agree with the author that there is practically no wear or undercutting at the slag line as is experienced when ganister or firebrick linings are employed, and, in practice, the lining wears thin by attrition.

The average sulphur reduction attained at Braintree was 68.5% (from 0.070% to 0.020%) when using 30 lb. of soda ash per ton of metal. This figure is an improvement of approximately 25% over ganister or firebrick linings.

No mention is made by the author of the life of linings made with calcined dolomite bonded with tar. I feel that some refer-

ence should have been made to this, which has a considerable bearing upon the economics of the process. The ladles used at Braintree had a lining 4 in. thick, the life of which was 178 heats with a throughput of 225 tons. At this stage the lining had worn back to approximately  $1\frac{1}{2}$  in. and was then considered to be worked out. Vitrification was found to be complete at the position in contact with the metal.

Unfortunately, as far as is known, no patching material is available for this type of lining, although tentative experiments have been made on a ladle using a magnesite cement bonded with sodium silicate. This could not be called a success, the few further heats obtained not justifying the cost of the magnesite cement.

Dealing with the cost of the process, we find that when using this type of ladle the cost is  $4\frac{1}{2}d.$  per ton. At first sight the cost appears to be rather in excess of that of ganister-lined ladles; this is not actually the position, however, as there is no patching or preheating, so that a saving of labour, raw material and gas is attained.

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#### AUTHOR'S REPLY.

The AUTHOR wrote in reply : I am grateful to Mr. Sanders for his comments and criticisms, particularly as he has based his remarks on his practical experiences in the use of basic-lined ladles.

The use of 6% of dehydrated tar and the heating of the mixture to about 70° C. before ramming are both matters of standard practice in the steel industry. It would be expected that a mixture containing a higher proportion of tar would be too spongy at such a temperature.

Mr. Sanders' confirmation of the resistance of "Basic" to the action of soda slags is valuable, as is also his report on the degree of desulphurisation obtained. This probably refers to treatment in ladles of about 2 tons capacity. In larger ladles even better results can be obtained, owing to the longer period during which the slag and metal are churned up together by the stream of metal entering the ladle. With certain grades of iron the sulphur content has been reduced to 0·015% or less.

The difficulty of patching basic-lined ladles is appreciated. It should be pointed out, however, that the same difficulty exists, perhaps in lesser degree, in patching linings of ganister and similar acid refractories. Time and again one has seen such patches washed away by the first heat of metal following the repair. It is understood that the producers of stabilised dolomite are devoting a considerable amount of attention to this problem, and the patching materials now available are better than those which were used when the author's investigations were begun. It is necessary, however, to stress the need for removing glaze from those portions of the lining which are to be patched. The best of patching materials applied on a glazed surface will peel off in a very short time.



# THE IRON-NICKEL PHASE DIAGRAM BY MAGNETIC ANALYSIS AND THE EFFECTS OF COLD-WORK.\*

By K. HOSELITZ, PH.D., F.I.N.S.P. (RESEARCH LABORATORY OF THE  
PERMANENT MAGNET ASSOCIATION, UNIVERSITY OF SHEFFIELD).

## SUMMARY.

The method of using measurements of magnetic saturation intensity of quenched and annealed iron-nickel alloys for the determination of equilibrium phases is briefly described. Previous studies of the thermal hysteresis phenomena and processes of phase changes have enabled a more complete equilibrium diagram of the iron-nickel system to be obtained than had before been possible. The slow rate of approach to equilibrium in these alloys necessitated the exploration of methods to expedite phase-change processes. With this aim in view, the magnetic saturation intensities of iron-nickel alloys which had been subjected to cold-work were examined over a wide range of temperatures. The methods of analysis developed in earlier work were applied to these experiments.

Whilst the annealing of cold-worked alloys gives inconclusive results, the effect of cold-work on quenched alloys produces marked changes in certain of the alloys, particularly between 29% and 35% of nickel, where the original single-phase alloys actually show a distinct separation into two phases. This can be seen by comparing their saturation-intensity/temperature relationships before and after cold-work. In alloys containing less nickel the changes are small, because these alloys are presumably not so far from their equilibrium state. In general, it can be concluded that cold-work alone brings about a certain amount of change towards equilibrium conditions, and in this case these experiments may prove of value in an attempt to determine the state and changes occurring in the alloys of nickel and iron at low temperatures.

## *Introductory.*

IN view of the practical importance of the iron-nickel alloys, the equilibrium phase diagram of this system has been the subject of a number of previous investigations. Almost all workers are agreed as to the general features of the equilibrium phase diagram. Face-centred  $\gamma$ -iron and nickel form a continuous solid solution over the whole range of concentrations, whilst body-centred cubic  $\alpha$ -iron dissolves only a limited amount of nickel. Consequently there exists a two-phase field, which becomes wider at low temperatures.

Two major difficulties are encountered in this binary system. In the first place there is the existence of irreversible changes which cause a variety of thermal hysteresis effects, the various critical temperatures on cooling and on heating being widely different, depending on the rate of change of temperature (Peschard<sup>(6)</sup>). The second difficulty lies in the extremely slow attainment of

\* Received July 30, 1943.

equilibrium coupled with the fact that phase changes take place at all temperatures down to room temperature and even lower. On the other hand, some transformations are instantaneous gliding processes, and the co-existence of these rapid and extremely sluggish changes is one reason for the complications arising in the determination of true equilibrium conditions. Two recent X-ray investigations (Bradley and Goldschmidt,<sup>(1)</sup> and Owen and Sully<sup>(5)</sup>) which have contributed greatly to the solution of the problem must here be mentioned.

The magnetic study of the iron-nickel system, made in recent years (Pickles and Sucksmith,<sup>(7)</sup> and Hoselitz and Sucksmith<sup>(8)</sup>), has succeeded in establishing a more complete equilibrium diagram than had hitherto been available. This was possible because the nature of the thermal hysteresis phenomena and the way in which phase-change processes take place had been studied and largely explained. A kinetic method, involving the extrapolation to equilibrium conditions from incomplete changes, has been evolved and found to be satisfactory. This is briefly outlined below, and experiments with cold-worked iron-nickel alloys, based on these former studies, are described in this paper.

### *The Magnetic Method of Analysis.*

It is known that the primary magnetic characteristics of a ferromagnetic material, the saturation intensity at high fields and the Curie temperature, are independent of physical properties and depend only on the chemical composition and the structure of the material. Thus a method for the accurate and quick measurement of these quantities can be a useful tool for obtaining information about phase changes in ferromagnetic alloys. A method which fulfills all the required conditions has been devised by Sucksmith<sup>(8)</sup> and has been fully described previously. It consists in measuring the force experienced by a ferromagnetic specimen in an inhomogeneous magnetic field. The specimen, which is surrounded by an electric resistance furnace during the whole experiment, can be brought to any temperature up to 1250° C., whilst replacement of the furnace by an appropriate vessel enables measurements to be taken down to -190° C. The use of a high magnetic field (about 16,000 oersteds) required to produce saturation demands the use of an electromagnet, and hence the necessarily limited region of high field and constant gradient calls for the use of a small specimen. This specimen can be in any form or shape, so long as it can be accommodated in the specimen holder, a cylindrical container of 2 mm. dia., 4 mm. long. Only a few milligrammes of the substance to be examined are necessary, and the force experienced by the average specimen is of the order of 5-10 g. weight. During the whole experiment the apparatus can be evacuated, so that there is no risk of oxidation or contamination. To take a measurement at room temperature requires only a few seconds, and a whole curve showing

the variation of  $\sigma$ , the magnetic intensity per unit mass, with temperature up to the Curie point can be obtained in about one hour for substances like iron or nickel. The accuracy is very high, and the values measured in routine work can be reproduced to less than one part in 100 at great speed. For precision measurements an accuracy of one in 400 is not difficult to attain.

Fig. 1 shows typical magnetic-intensity/temperature ( $\sigma-T$ ) curves for single-phase specimens. Curve (a) was obtained for a

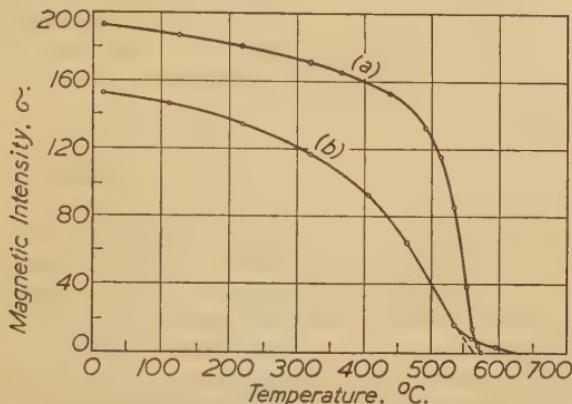


FIG. 1.—Magnetic-Intensity/Temperature Curves of Quenched Alloys.  
(a) 23% nickel,  $\alpha$  phase (body-centred cubic); (b) 50% nickel,  $\gamma$  phase (face-centred cubic).

23% nickel alloy in the single-phase  $\alpha$  state (body-centred cubic); curve (b) is for a 50% nickel alloy, which is pure  $\gamma$  (face-centred cubic). If more than one phase is present the curves are not so simple and show inflexions, but the meaning of these curves can always be interpreted without difficulty and examples of such curves are given in Fig. 2. It has been established that the tempera-

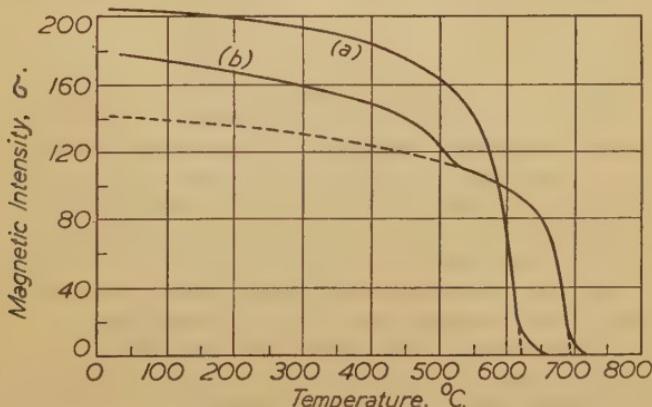


FIG. 2.—16% Nickel Alloy. (a) Quenched, pure  $\alpha$ ; (b) after 18 days' anneal at 525°C.,  $\alpha + \gamma$ .

ture of magnetic transition—which either may be a true Curie point and therefore reversible or may be due to a breakdown of the ferromagnetic lattice and be irreversible on cooling—is characteristic of the composition of a phase, whilst the relative intensity at a fixed temperature is a quantitative measure of the amount of a phase present in an alloy. In most cases an accurate analysis of the alloy under investigation is obtainable from these relations (Fig. 2). It is obvious that the method which only necessitates a few seconds for an observation is suitable for tracing out the change during a heat treatment, and is therefore a valuable addition to the available methods for studying phase-change processes.

### *The Iron-Nickel Phase Diagram for Equilibrium Conditions.*

The study of the iron-nickel system was made with pure alloys ranging from 3 to 50 atomic-% of nickel, which were obtained from Dr. A. J. Bradley, F.R.S., and the purity and preparation of which had been given by Bradley and Goldschmidt.<sup>(1)</sup> Specimens were prepared in the shape of small prisms cut out from the lumps and in all cases were heated to 1000° C. for 4 hr., quenched in cold water and subsequently cooled to -180° C. for 48 hr. This standard treatment was used to ensure that all specimens were in a single-phase state (in the following called the quenched state). Alloys with more than 33% of nickel remained wholly face-centred cubic ( $\gamma$ ) even through quenching, whilst below this limit they changed irreversibly into the body-centred cubic  $\alpha$  state by instantaneous transformation. The  $\alpha$  state is the most suitable basis for annealing experiments; the  $\gamma$  lattice is even more difficult to break up, as has been shown by Bradley and Goldschmidt.<sup>(1)</sup> Curves showing the change of  $\sigma$  with temperature were recorded for all these alloys, two examples being given in Fig. 1.

Specimens of each alloy were subjected to annealing treatments at various temperatures for suitable periods and their  $\sigma$ - $T$  curves were recorded and examined.

If during annealing an alloy has undergone a change, this will manifest itself in its  $\sigma$ - $T$  curve being different from that of the quenched alloy. Any  $\gamma$  phase formed out of the original single-phase  $\alpha$  state will alter the intensity at room temperature and show its own Curie temperature, whilst the magnetic transition of the remainder will be increased owing to its lower nickel content. Not only can these characteristics be used in order to determine in which state a specimen is, whether single-phase,  $\alpha$  or  $\gamma$ , or two-phase, but also the composition of each phase can be calculated from the transition temperature, whilst the magnetic intensity gives a measure of the amounts of the two phases present. The composition can be determined in the case of an  $\alpha$  phase to within  $\pm 1\%$  of nickel, and in the case of a  $\gamma$  phase, where the transition is less defined (see curve (b), Fig. 1), to within  $\pm 1-3\%$  of nickel. Fig. 2

gives an example of a single-phase alloy breaking up into its constituents during annealing, curves typical of those obtained in this investigation; curve (a) shows a 16% nickel alloy as quenched, pure  $\alpha$  (body-centred cubic), whilst curve (b) is the  $\sigma$ - $T$  curve for the same alloy after 18 days' anneal at 525° C. Examination of this curve shows that the alloy had separated into two phases, the  $\sigma$ - $T$  curves of which are superimposed. The composition of these two phases can be determined from the two magnetic transition temperatures, at 520° and 700° C. These correspond to 26% and 9% of nickel, respectively.

In this system phase changes are very sluggish, and this sluggishness necessitated the development of a kinetic method, *i.e.*, one which would enable the true equilibrium conditions to be extra-

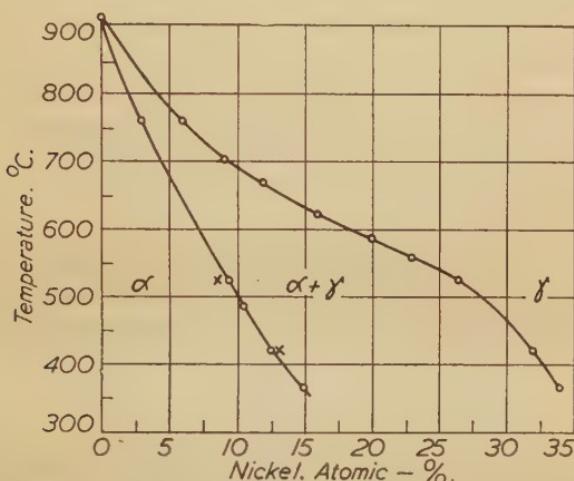


FIG. 3.—Equilibrium Phase Diagram of the Iron-Rich Nickel-Iron Alloys.

polated from experiments made over shorter periods in which equilibrium had not been attained. The procedure consisted in examining alloys which had been annealed at certain temperatures for various times so as to try to find the mechanism and speed of the processes involved and hence to determine the final state.\*

The true equilibrium diagram of the iron-nickel alloys extending down to 365° C. is shown in Fig. 3. This diagram was obtained as a result of the solution of the two previously mentioned difficulties, *i.e.*, the explanation of the nature of the thermal hysteresis of the alloys in relation to the phase changes, and the adoption of the kinetic method and extrapolation of not completed changes to true equilibrium conditions (Pickles and Sucksmith,<sup>(8)</sup> and Hoselitz and

\* It may be pointed out that the kinetic method is applicable in principle to all similar problems and does not depend on the actual experimental procedure, *i.e.*, whether electrical, mechanical, crystallographic or magnetic characteristics are observed.

Sucksmith<sup>(3)</sup>). Information was also obtained from the result of the investigation on the mechanism of phase segregation of a quenched alloy into a two-phase alloy. It has been shown that in a quenched single-phase  $\alpha$  alloy, annealed at a temperature falling within the two-phase field, the  $\gamma$  phase crystallises out of the matrix in its equilibrium concentration, whilst the residue changes its composition continuously and uniformly until equilibrium is finally reached. It was also possible to formulate quantitatively the processes of segregation and, from the rate of approach to equilibrium, to estimate the time required for changes to be completed. These times are of the order of 40 years at 300° C., 10 years at 325° C. and still about one year even at 365° C.

### *The Application of Cold-Work.*

Since, according to the foregoing evidence, further annealing experiments were not to be expected to yield results, and indeed alloys treated for long periods at 420° and 365° C. showed only very slight changes, the extension to lower temperatures was sought in the application of cold-work. It was hoped that a study of the effects of this cold-work would result in a speeding-up of the attainment of equilibrium conditions.

It is well known from previous work (*e.g.*, Fry,<sup>(10)</sup> and Turner and Jevons<sup>(9)</sup>) that in some alloy systems cold-working after quenching increases the rate of precipitation and accelerates the attainment of equilibrium of the phase changes. It was therefore thought probable that in the iron-nickel system the application of cold-work might have a similar effect, thus enabling the annealing times to be reduced and facilitating the approach to equilibrium in the lower-temperature region. Preliminary experiments were carried out simultaneously with the study of the non-cold-worked alloys (referred to in what follows as "normal"). The description and discussion of these experiments on cold-worked alloys are given below.

The iron-nickel alloys used were the same as those investigated before. These were brought into the quenched state. The specimens were then placed on a cast-steel anvil and hammered alternately on adjacent long faces until their length had increased from 4 mm. to about 12 mm. Alloys with a low nickel content and those with more than 33% of nickel were found to be more ductile than those of intermediate percentages (16–33%), the latter being liable to crack and flake. After this somewhat crude treatment, for which it was impossible to make a quantitative estimate of the amount of cold-work performed on the lattice, it can be assumed that the specimens were severely cold-worked and that the lattice was very distorted. It is quite reasonable to suppose that in this state diffusion takes place more readily than in an undistorted lattice and therefore that changes other than instantaneous transformations are accelerated. The alloys in the cold-worked condition were then

annealed at various temperatures, and finally the variation of their magnetic intensity with temperature was recorded. The annealing temperatures and times chosen were those for which results on normal alloys were known from previous work,<sup>(3)</sup> so that the effect of the cold-work could easily be determined by comparison. The results of these experiments seem in many cases to confirm the view that the attainment of equilibrium is accelerated by cold-work, yet in others the results are quite unexpected.

#### *Annealing Experiments with Cold-Worked Alloys.*

For the first annealing treatment 18 days at 525° C. was chosen, since complete results of this treatment on normal alloys had been obtained previously. The comparison of the two sets of  $\sigma$ - $T$  curves revealed that the cold-worked specimens had separated into the same

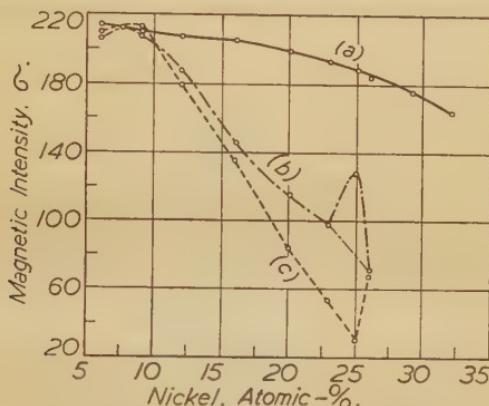


FIG. 4.—Variation of Magnetic Saturation Intensity with the Nickel Content in Variously Treated Iron-Nickel Alloys. (a) Quenched; (b) quenched and subsequently annealed at 525° C. for 18 days; (c) quenched, cold-worked and subsequently annealed at 525° C. for 18 days.

components as the normal alloys, this being observed by the agreement of the respective transition temperatures. The magnetic saturation intensity, which is a measure of the amount of a ferromagnetic constituent, was lower in the cold-worked specimens; this difference in  $\sigma$  increased with increasing nickel content up to 25% of nickel. Fig. 4 shows  $\sigma$  for quenched, for normal annealed and for cold-worked annealed alloys after 18 days at 525° C. In the region of 25% of nickel the magnetic intensities of annealed normal and cold-worked alloys show marked differences. In addition to the two equilibrium phases, the normal alloys here contain a third constituent, of the composition of  $Fe_3Ni$ , which is absent from the cold-worked alloys. Furthermore, the equilibrium boundary for the  $\gamma$  phase at 25% is just above 525° C. In view of this fact the following tentative explanation is put forward, though admittedly it is only

one of several possibilities: The existence of a superlattice at 25% of nickel is not unlikely, and it is assumed that this is face-centred cubic and hence belongs to the  $\gamma$  phase. If this is the case, this ordered structure should be formed in a not cold-worked quenched alloy during subsequent annealing at 525° C., and hence it should appear in the  $\sigma-T$  curves as a separate phase. At other annealing temperatures, where the equilibrium composition of the  $\gamma$  phase is different from 25%, this ordered constituent would not be formed, as is borne out by experiment. In a cold-worked alloy, however, a  $\gamma$  phase of much higher nickel content than that of  $\text{Fe}_3\text{Ni}$  is precipitated (evidence for this is given below), and the formation of a superlattice from this during subsequent annealing at any temperature would be unlikely, since changes in the  $\gamma$  phase, as has been said before, are very sluggish indeed. A visual example of the possibility of detecting the presence of an additional third constituent in a specimen by the magnetic method is given in Fig. 5,

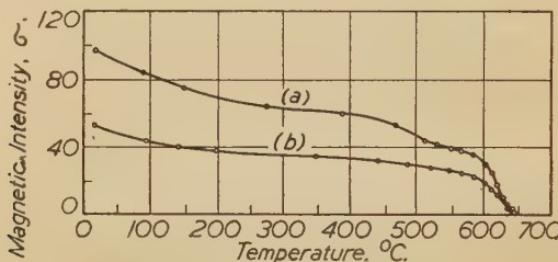


FIG. 5.—Magnetic-Intensity/Temperature Curves of 23% Nickel Alloy Annealed at 525° C. (a) Normal alloy; (b) cold-worked alloy.

which shows data on 23% nickel alloys. In curve (a), the  $\sigma-T$  curve for a normal alloy, the presence of three constituents reveals itself by the three different transition temperatures, the evidence being similar to that obtained in alloys with two constituents. The three constituents can be identified as the two equilibrium phases, having transition temperatures of about 170° and 640° C., and the 25% nickel constituent, with a transition temperature of about 530° C. Similar curves were obtained for 25% nickel alloys. Above 26% of nickel the normal as well as the cold-worked alloys are in the face-centred cubic  $\gamma$  state after annealing at 525° C., and no difference between them can be detected in their  $\sigma-T$  curves.

Another set of specimens, ranging from 20% to 40% of nickel, was annealed for 18 days at 490° C. Here, surprisingly, the  $\sigma-T$  curves of the cold-worked alloys were very little different from those of the normal alloys, although there were some slight changes that seem to suggest that the former had approached nearer to equilibrium than the latter. The differences are, however, not very marked, although it would have been expected that at the lower temperatures the effect of cold-work should have increased.

*The Effect of Cold-Work on Quenched Alloys.*

As it would have taken several months to reproduce the heat treatments that the normal alloys had received at the temperatures below 490° C., and because the results of the above experiments with cold-worked alloys were yielding complex results, it was decided to examine the state of the cold-worked specimens before annealing and to compare it with that of normal quenched specimens. These experiments were expected to give more direct evidence of the actual effect of cold-work and to show whether the original effect of cold-work could be detected in the  $\sigma-T$  curves. A set of specimens was therefore carefully quenched and cold-worked in the way described above. Their  $\sigma-T$  curves were then determined and compared with those of normal quenched alloys. This comparison yielded the following information.

At the iron-rich end, up to 12% of nickel, the cold-work did not cause any change. This is presumably due to the fact that these alloys are solid solutions and we should therefore not expect any change in  $\sigma$  due to lattice distortions, because the magnetic intensity at the high fields used here (about 16,000 oersteds) is independent of physical properties such as strain.

Between 12% and 23% of nickel cold-work causes an increase in saturation intensity without altering the magnetic transition temperature. It has been established that the temperature of the magnetic transformation is the most critical factor for the determination of the nickel content of these alloys; hence if this temperature remains unaffected by cold-work, one can conclude that the nickel concentration in the bulk of the alloy has not altered. Nevertheless, an increase in  $\sigma$  is observed, and an inspection of the  $\sigma-T$  curves shows also that the magnetic transition is not so sharp as it is in normal alloys. This may be caused by some rearrangement of atoms in some part of the lattice, just as the presence of a 25% nickel superlattice causes an increase in  $\sigma$ , and it is suggested that these phenomena are the magnetic evidence of the changes within the lattice caused by atomic movement preparatory to precipitation. Such phenomena have been detected by many workers (*e.g.*, Merica,<sup>(4)</sup> Gayler and Preston,<sup>(2)</sup> and Gayler<sup>(11)</sup>). Fig. 6 shows an example of the  $\sigma-T$  curves of 12% nickel normal and cold-worked alloys. It is probable that at ordinary temperatures these alloys are in a two-phase field, as cold-work seems to initiate phase segregation, and it is therefore suggested that the  $\alpha$  boundary may lie in the neighbourhood of 12% of nickel at room temperature.

In the region of 25% of nickel cold-worked alloys undergo a sharper magnetic transition than normal alloys, again without a change in the actual temperature at which the transition is completed. This can be understood if it is assumed that traces of an ordered structure of  $\text{Fe}_3\text{Ni}$  exist in the quenched alloy and that these traces are broken up by cold-work. The small increases in  $\sigma$  which

is found here seems to indicate that the postulated traces of a third constituent, when broken up, raise the amount of  $\alpha$  phase already present. The changes brought about by cold-work are, however,

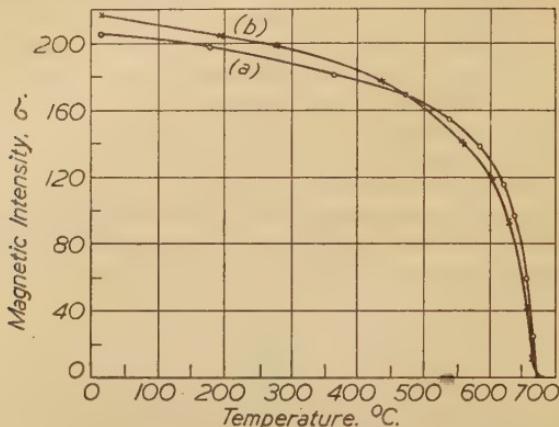


FIG. 6.—Magnetic-Intensity/Temperature Curves of 12% Nickel Alloy, quenched. (a) Normal alloy; (b) cold-worked alloy.

very small, as illustrated in Fig. 7, which refers to a 26% nickel alloy.

For alloys containing from 29% to 35% of nickel, however, cold-work does actually cause the precipitation of two phases from the

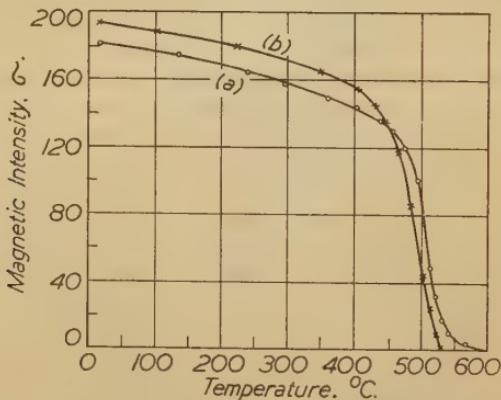


FIG. 7.—Magnetic-Intensity/Temperature Curves of 26% Nickel Alloy, quenched. (a) Normal alloy; (b) cold-worked alloy.

original single-phase alloy. In Fig. 8 are reproduced  $\sigma-T$  curves for (a) the normal 32% nickel alloy and (b) for the cold-worked alloy; the inflexion in the  $\sigma-T$  curve can only be interpreted as showing the presence of two phases. By means of the method

described previously, the nickel content of the two phases into which the original single-phase alloy (Fig. 8) has split by the application of cold-work can be determined. The other alloys in this region also show that segregation of two phases takes place during cold-work. In all the  $\sigma-T$  curves of these alloys, which are unmistakably two-phase after cold-work, the intensity at room temperature

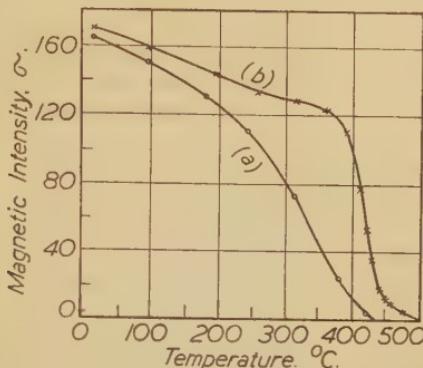


FIG. 8.—Magnetic-Intensity/Temperature Curves of 32% Nickel Alloy, quenched. (a) Normal alloy; (b) cold-worked alloy.

is due to the two phases, one  $\alpha$ , with a lower nickel content than the original alloy and hence a higher  $\sigma$ , and the other  $\gamma$ , with a higher nickel content than the original alloy. It is clear that if enough of the new  $\alpha$  phase is present, the room-temperature intensity may increase appreciably. The changes in these alloys are summarised in Table I.

TABLE I.—Iron-Nickel Alloys. Lattice Forms and Nickel Contents of Phases before and after Cold-Working.

Nickel Content of Alloy. %.	Lattice Form.	Lattice Forms from $\sigma-T$ Curves.	After Cold-Work.	
			Nickel in Phase Produced. %.	
			$\alpha$ .	$\gamma$ .
29	$\alpha$	$\alpha$	27	...
30.5	$\alpha$	$\alpha$	28.5	...
32	$\alpha$	$\alpha + \gamma$	30.5	34
33.5	$\gamma$	$\alpha + \gamma$	Very little	33.5
35	$\gamma$	$\alpha + \gamma$	Very little	35

It is quite clear that in all these alloys cold-work has caused precipitation. Even in the 29% and 30.5% nickel alloys, in which the  $\gamma$  phase could not be detected in the  $\sigma-T$  curves after cold-

work, precipitation must have taken place, because the increased transition temperature of the  $\alpha$  phase indicates an appreciably lowered nickel content of this phase. This could not have taken place without the surplus nickel being taken up by the other phase. In view of the fact that precipitation occurs in the alloys, the suggestion made above, that in alloys with 12–23% of nickel processes preparatory to precipitation have taken place, seems justified. It is well known that precipitation causes hardening at a certain state of dispersion, and it seems probable that in work-hardening the processes are similar to the phenomena of precipitation-hardening, in so far as cold-work initiates and causes precipitation, as shown in this research.

If one accepts the evidence that cold-work hastens the approach to equilibrium, then it is justifiable to extrapolate the equilibrium diagram of the iron-nickel system to lower temperatures, in which case the region of 29–35% of nickel lies in the two-phase field. One would therefore expect that alloys with more than 29% of nickel would be affected by cold-work, as is borne out by experiment.

In the region above 35% of nickel, the alloys are all in the single-phase  $\gamma$  state, and it is extremely difficult to bring about a change in this structure. Cold-work also does not affect alloys in this region, but it is not impossible that the  $\gamma$ -phase boundary at room temperature lies above 35% of nickel. The experimental evidence seems to show that it does not lie below this limit.

The author wishes to record his thanks to Professor W. Sucksmith, F.R.S., for his continued advice and help, to the British Electrical and Allied Industrial Research Association for a grant, and to Professor A. M. Tyndall, F.R.S., for putting at his disposal the facilities of the Physical Laboratory of the University of Bristol, where the work was carried out.

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## CORRESPONDENCE.

Dr. A. H. SULLY (Mond Nickel Co., Ltd., Birmingham) wrote : I have read with considerable interest this paper and also the earlier papers by Hoselitz and Sucksmith<sup>1</sup> and Pickles and Sucksmith<sup>2</sup> relating to the application of magnetic analysis to the elucidation of the constitutional aspects of iron-nickel alloys. The author is to be commended upon the development of an interesting and novel method of approach to the study of this alloy system, which is distinguished by the complexity of its non-equilibrium conditions in spite of its simple equilibrium diagram. At the same time, I am not convinced that the author has justified his claim that the equilibrium diagram presented represents true equilibrium conditions. In particular, there are disturbing differences in the location of the  $\alpha/(\alpha + \gamma)$  and the  $(\alpha + \gamma)/\gamma$  boundaries, particularly at temperatures below 600° C., between the earlier X-ray work of Jette and Foote,<sup>3</sup>

TABLE A.— $\alpha/(\alpha + \gamma)$  and  $(\alpha + \gamma)/\gamma$  Boundaries (Nickel, Atomic-%).

Temperature. °C.	Owen and Sully.	Jette and Foote.	Bradley and Goldschmidt.	Hoselitz.
$\alpha/(\alpha + \gamma)$ Boundary.				
600	3.5	...	5.5	7
557	4.0	4.22	6.5	8
500	5.0	...	7.0	10
496	5.0	6.07	7.0	10
400	6.5	...	8.0	13
350	5.8	...	8.5	15.5 *
$(\alpha + \gamma)/\gamma$ Boundary.				
600	14	...	6.5	18.5
500	27	...	25.5	28.0
456	34	33.4	26.0	30.0
400	41.5	...	26.5	33.0
350	49	...	39.0	34.0 *

\* Extrapolated value.

<sup>1</sup> *Proceedings of the Royal Society*, 1943, A., vol. 181, p. 303.

<sup>2</sup> *Proceedings of the Royal Society*, 1940, A., vol. 175, p. 331.

<sup>3</sup> *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1936, vol. 120, p. 259.

Owen and Sully<sup>1</sup> and Bradley and Goldschmidt<sup>2</sup> on the one hand and the magnetic analyses on the other. The locations of these boundaries for the various investigations are given in Table A. It will be seen that the values reported in the present paper place the  $\alpha/(\alpha + \gamma)$  boundary appreciably to the nickel-rich side of the boundary proposed by Owen and Sully, whereas the  $(\alpha + \gamma)/\gamma$  boundary, particularly at temperatures below 500° C., is placed considerably to the iron-rich side of Owen and Sully's boundary.

Now, the X-ray data on which the latter values were based were determined on severely cold-worked filings from a large number of high-purity alloys which initially were in a homogeneous single-phase condition; that is, the alloys containing up to 28% of nickel were all in the supersaturated  $\alpha$ -phase condition produced by quenching from temperatures of above 600° C., whilst the alloys containing more than 28% of nickel contained only the  $\gamma$  phase. Thus, the  $\alpha/(\alpha + \gamma)$  boundary was determined on alloys which initially were confirmed to be single-phase  $\alpha$ , while the  $(\alpha + \gamma)/\gamma$  boundary at temperatures of 500° C. and below was determined on alloys which initially were confirmed to be single-phase  $\gamma$ . The location of the phase boundaries was determined from the appearance of lines due to the  $\gamma$  phase in the X-ray spectra of the former alloys and the appearance of lines due to the  $\alpha$  phase in X-ray spectra of the latter. The amount of second phase, particularly of the  $\alpha$  phase in alloys initially single-phase  $\gamma$ , was found to increase with the time of soaking at temperature, and corresponding changes of lattice parameter were measured after a wide range of soaking times and cooling rates. In particular, at 350° C. after a heat treatment of 186 days on severely cold-worked filings the  $\alpha$  lattice was so well formed that it was possible to measure its lattice parameter accurately in alloys containing up to 41.5% of nickel, that is, in alloys containing up to 7.5% in excess of the boundary advanced by the present author at this temperature. At higher nickel contents the  $\alpha$  phase was still detectable, and after 265 days at 300° C. it was present in an alloy containing 50.9 atomic-% of nickel. Determinations by this method are obviously likely to give maximum nickel contents for the  $\alpha/(\alpha + \gamma)$  boundary and minimum nickel contents for the  $(\alpha + \gamma)/\gamma$  boundary, since only alloys in which the second phase was present in amounts large enough to be definitely identified in X-ray spectra were assigned to the two-phase region.

This large discrepancy between the results of the magnetic and the X-ray methods deserves further consideration. If, as the author claims, the Curie temperature, and hence the composition, of the separating phase is accurately determinable from the magnetic-intensity/temperature curve, the explanation is not immediately obvious, but is probably involved with the peculiarities associated with the atomic migrations in alloys of this type at low tempera-

<sup>1</sup> *Philosophical Magazine*, 1939, vol. 27, p. 614.

<sup>2</sup> *Journal of The Iron and Steel Institute*, 1939, No. II., p. 11 P.

tures. A clue which may explain the difference between the X-ray and magnetic measurements of the  $(\alpha + \gamma)/\gamma$  boundary at temperatures below 500° C. is, perhaps, provided by lattice-parameter measurements reported by Owen and Sully.<sup>1</sup> Lattice-parameter/composition curves for the  $\gamma$  phase for a variety of heat treatments at 400° C. are given in Fig. A. The curve *ABCDME* refers to a heat treatment of 132 hr. at 400° C. followed by rapid quenching, while the curve *KLDME* refers to a heat treatment of 132 hr. at 400° C. followed by cooling to room temperature over a period

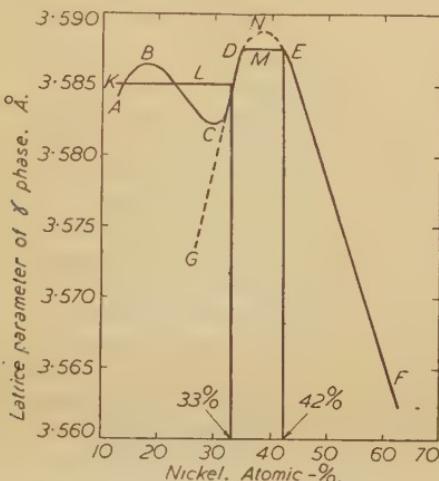


FIG. A.—Lattice-Parameter/Composition Curves for Alloys Heat-Treated at 400° C.

of 96 hr. The dotted curve *GCDNEF* is the lattice-parameter/composition curve for single-phase  $\gamma$  alloys. It cannot be claimed that either of these curves represents equilibrium conditions, in which case the lattice parameter would be constant in two-phase alloys, but they throw an interesting light on the method of approach to equilibrium, particularly in the case of the slowly cooled alloys. Thus, for the slowly cooled alloys, those with less than about 33% of nickel have a constant lattice parameter intersecting the single-phase lattice parameter curve at approximately 33% nickel, thence following the single-phase curve between 33 and 35% nickel and then having another constant but different lattice parameter intersecting the single-phase curve at 42% nickel. It is significant that the magnetic-analysis method gives a solubility limit of 33%, agreeing with the first straight-line portion of the lattice-parameter relation, while X-ray analysis gives a limit at 42% nickel, corresponding to the second straight-line portion of this relation. May this not mean that the abstraction of iron from the lattice to form

<sup>1</sup> *Philosophical Magazine*, 1941, vol. 31, p. 314.

$\alpha$  phase in alloys containing less than 33% of nickel occurs in two stages, with a fairly well-defined metastable intermediate "sub-equilibrium" phase? The first stage in the trend to equilibrium at 400° C. would thus correspond to the production of a metastable  $\gamma$  phase containing 33% of nickel, while further soaking results in a breakdown of this phase with the formation of more  $\alpha$  phase and the equilibrium 42% nickel  $\gamma$  phase. It may be significant in this connection that the 33% nickel level corresponds to the composition Fe<sub>2</sub>Ni.

I shall be interested to hear Dr. Hoselitz' reaction to this possible explanation of the discrepancies between the various investigations in locating the ( $\alpha + \gamma$ )/ $\gamma$  boundary. It would appear that the X-ray investigation has achieved a closer approach to equilibrium than that described in the present paper. This is almost certainly involved with the effect of cold-work on the speed of approach to equilibrium in these alloys, which is probably more effective in the case of fine filings than in cold-worked massive metal. The greater ease with which fine particles may permit volume changes accompanying phase changes to occur may be an important factor. It would be interesting in this connection to discover whether Dr. Hoselitz could obtain the same results on compacts obtained by pressing to a suitable density samples of cold-worked filings of these alloys.

Dr. S. A. MAIN (Messrs. Hadfields, Ltd., Sheffield) wrote : Has the author considered the possibility in the experiment charted in Fig. 8 that, in the course of heating, the splitting of the phases found in the cold-worked material may have developed further? It does not seem possible otherwise, unless by the occurrence of still other transformations, to account for the increasing departure of curve (b) from curve (a) up to about 350° C.

With reference to the remark on p. 204 P, is it really well known that precipitation causes hardening at a certain state of dispersion, or is this still only a theory, though receiving wide acceptance? With regard to certain ferrous alloys the writer has suggested<sup>1</sup> a more rational explanation of the hardening based on known physical facts rather than on the purely imaginative mechanical effect of invisible particles.

#### AUTHOR'S REPLY.

The AUTHOR wrote in reply : I am very interested in the points raised by Dr. Sully, which open up important general aspects of the work on alloy systems.

As far as the disturbing differences tabulated in Table A of Dr. Sully's contribution are concerned, it can be pointed out that the

<sup>1</sup> *Metal Treatment*, 1938-39, vol. 4, Winter issue, p. 158.

location of the phase boundaries by Jette and Foote<sup>1</sup> and by Bradley and Goldschmidt<sup>2</sup> was only a tentative suggestion, as expressed by those authors themselves. This fact alone is a very good indication of the complexity and the difficulties encountered with in the iron-nickel system. Furthermore, by inspecting the experimental results of Bradley and Goldschmidt it can be seen that the phase boundaries proposed by Hoselitz and Sucksmith can be fitted without contradiction in their work, except for one questionable point at 450° C., 7·6 atomic-% nickel. However, this statement leaves the difference between Owen and Sully's<sup>3</sup> and Hoselitz and Sucksmith's<sup>4</sup> work unexplained. In the case of our own work the phase boundaries were determined on solid specimens by extrapolation to infinite times of anneal. As far as I am aware this was the first attempt to overcome the difficulties of slow phase changes at low temperatures in the iron-nickel system. We were able to indicate the mechanism of phase segregation in specimens which were in the distorted  $\alpha$  state. This was achieved by quenching all specimens in liquid air, for we have found that specimens which were in the  $\gamma$  state before annealing approached equilibrium considerably more slowly. By means of measurements on specimens brought into the  $\alpha$  state by quenching in liquid air the following phase-change mechanism was established: During annealing, if the specimen is in the  $\alpha + \gamma$  field at the temperature chosen, the  $\gamma$  phase crystallises out at a fixed composition, and as this increases in amount the remaining  $\alpha$  phase continuously changes its composition until equilibrium is established. In no case could a change in composition of the  $\gamma$  phase, even after prolonged annealing, be observed. In this way, extrapolation to infinite time was possible. As pointed out by Hoselitz and Sucksmith, the time required for the  $\alpha$  phase to change its composition to a value half-way between the original and the equilibrium value would be one year at 365° C. and 10 years at 325° C. It is possible that this "final" state is a metastable one, but in that case it is evident that at low temperatures true equilibrium can be reached only after times of very long duration indeed. It is true, however, that if the  $(\alpha + \gamma)/\gamma$  boundary at 400° C. were indeed situated at 42% nickel, the consequent necessary change in the composition of the equilibrium  $\alpha$  phase would correspond more closely with Owen and Sully's results.

I would suggest that the reasons for the difference in results are as follows: In the first place we attempted to approach equilibrium from the  $\alpha$  state by quenching in liquid air, whilst Owen and Sully started from the  $\gamma$  state in their phase determination. Further, as mentioned above, in solid  $\gamma$ -phase specimens no change at all

<sup>1</sup> *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1936, Iron and Steel Division, vol. 120, p. 259.

<sup>2</sup> *Journal of The Iron and Steel Institute*, 1939, No. II., p. 11 P.

<sup>3</sup> *Philosophical Magazine*, 1939, vol. 27, p. 614.

<sup>4</sup> *Proceedings of the Royal Society*, 1943, A., vol. 181, p. 303.

could be observed during annealing, and it is reasonable to suggest that the reactions in filings take a different course from those in the solid metal. The reasons for this may be the severe effect of cold-work as well as surface effects and other co-operative phenomena. I think that Dr. Sully overestimates the validity of conclusions to be reached by experiments on powdered specimens. However, it would be interesting to see X-ray results of experiments with solid specimens, since these are more likely to allow definite conclusions than magnetic measurements on powders, which present considerable experimental difficulties.

I think it is of general interest to mention that the method of using measurements of the magnetic saturation intensity at high fields at various temperatures provides a new tool in the study of ferromagnetic alloy systems. It provides facilities for the accurate study of conditions in solid specimens of alloys during heat treatment. The measurement of the intensity takes only a few seconds, and consequently no change in the specimens during the actual measurement can take place. A full  $\sigma$ - $T$  curve, which usually allows a reasonably accurate quantitative determination of all the phases present, involves only a time short enough to prevent changes from taking place during the experiment. According to recent evidence, in some cases it is only necessary to take measurements at two or three different temperatures,<sup>1</sup> and, since the apparatus allows very quick temperature changes, the time during which a prepared specimen is subject to elevated temperatures can be very short indeed—I should say of the order of a few minutes.

Thus it can be seen that, whilst this new method is not yet fully tried out, it obviously adds to our methods of attack on equilibrium conditions and especially on the questions of approach to equilibrium in ferromagnetic alloys.

Concluding, I would like to thank Dr. Sully for his very interesting comments. The fact that not only two different methods give different results but also that in the studies by means of one experimental method, such as X-rays, there are such differences as are indicated by Dr. Sully in Table A opens the question of further work. Lastly, it should be emphasised that the magnetic method is capable of considerable development, and I hope that this discussion may stimulate further work along these lines.

In reply to Dr. Main I would like to say that I have considered the possibility in the experiment charted in Fig. 8 that, in the course of heat-treating, the splitting of the phases found in the cold-worked material may have developed further. By observing the magnetic intensity of all samples after the  $\sigma$ - $T$  curve had been taken any such development would have been noticeable by the new value of  $\sigma_{RT}$ . In no case was it possible to find any difference in the specimen before and after the experiment. This fact is not surprising, since

<sup>1</sup> In these cases the number of points required depends on the number of magnetic phases present, and is equal to that number.

the curves were taken as quickly as possible in order to prevent changes in the course of heating (see reply to Dr. Sully). It is, however, quite possible to account for the increasing departure of curve (b) from curve (a) up to 350° C. as is explained in the paper. I would add that, during the course of a more detailed analysis of the character of  $\sigma$ - $T$  curves as a function of the composition of the phase, quantitative agreement with the views expressed in the paper could be found. The publication of this work is still in preparation.

With reference to the second point which Dr. Main raised I do not feel competent to argue about the validity of the theory of precipitation-hardening. I would, however, point out that the evidence collected in the case of aluminium alloys (Gayler and Preston, &c.<sup>1</sup>) and in many other alloys, including ferrous alloys (*e.g.*, Köster<sup>2</sup>), has to be taken into serious consideration. In the paper quoted by Dr. Main I find, however, that he does not reject the rational character of the theory of precipitation-hardening in general but that he explains the hardening in steels containing carbon by means of a slightly different mechanism. In view of the fact that the nickel-iron alloys in my work were free from carbon, the formation of carbides necessary for the mechanism as proposed by Dr. Main is excluded. I have not tested whether nickel-iron hardens during precipitation or as a result of cold-work. But, since cold-work and precipitation in certain alloys undoubtedly cause hardening, I have suggested that the precipitation taking place during cold-work may be an important factor in work-hardening, since I could prove that in iron-nickel alloys cold-work does cause precipitation.

<sup>1</sup> Gayler and Preston, *Journal of The Institute of Metals*, 1929, vol. 41, p. 191. Gayler, *ibid.*, 1937, vol. 60, p. 75.

<sup>2</sup> *Stahl und Eisen*, 1933, vol. 53, p. 849.



# THE OCCURRENCE OF THE CARBIDE PHASE IN HIGH-SILICON IRON-CARBON ALLOYS.<sup>1</sup>

BY J. E. HURST, D.MET., AND R. V. RILEY, B.Sc., PH.D. (MESSRS. BRADLEY AND FOSTER, LTD., DARLASTON).

(Figs. 1 to 10 = Plates IV. and V.)

## SUMMARY.

The authors record the presence of a carbide constituent in commercial iron-carbon-silicon alloys containing 10–15% of silicon. This carbide is found to be present on rapid solidification of the alloy followed by a quick rate of cooling in the solid state. On annealing, the carbide constituent decomposes with the formation of "fine graphite" and presumably silico-ferrite. The influence of alloying elements upon the stability of the carbide was investigated and found to be similar to the action of the same elements on the cementite in low-silicon iron-carbon alloys. The true identity of the carbide has not been established, but it is shown that it cannot be regarded as pure cementite.

## *Introduction.*

In the iron-silicon binary system the pure stable alloys containing less than 15.5% of silicon consist of a single phase, the  $\alpha$  solid solution, generally referred to as silico-ferrite. In the stable iron-carbon-silicon ternary system at room temperature it is generally agreed that the  $\alpha$  solid solution persists over a similar range of silicon percentages accompanied by more or less graphite, depending upon the carbon content of the alloy. The occurrence of a carbide phase has been recorded in commercial iron-carbon-silicon alloys of high silicon content following upon rapid cooling from the molten state. Andrew,<sup>2</sup> working with an alloy containing 9.86% of silicon and 2.52% of carbon made from commercial pig iron and 95% ferro-silicon, showed the existence of a carbide constituent in this alloy after quenching from just below the melting point, then allowing to melt and quenching again in the plastic condition. Kříž and Pobořil<sup>3</sup> in their examination of similar alloys reported the presence of a carbide phase in all the chill-cast specimens containing 9.63–10.28% of silicon with carbon contents of from 0.22% to 1.35%. These specimens prepared from commercial materials contained manganese from 0.28% to 0.47% and phosphorus and sulphur in amounts of less than 0.10% and 0.035%, respectively.

<sup>1</sup> Received August 12, 1943.

<sup>2</sup> J. A. Andrew, *Iron and Steel Institute, Carnegie Scholarship Memoirs*, 1916, vol. 7, pp. 1–17.

<sup>3</sup> A. Kříž and F. Pobořil, *Journal of The Iron and Steel Institute*, 1930, No. II., pp. 191–211; 1932, No. II., pp. 323–348.

The object of this present work was to investigate the occurrence of the carbide phase in commercial iron-carbon-silicon alloys of higher silicon content.

TABLE I.—*Chemical Compositions of Specimens.\**

Specimen No.	Si. %.	C. %.	Mn. %.	P. %.	S. %.	Other Elements.
1	<u>10·5</u>	1·00	0·74	0·050	0·06	Ni. 0·25
2	15·2	<u>0·50</u>	0·64	0·034	0·04	0·28
3	15·1	<u>0·16</u>	<u>0·33</u>	0·025	...	...
4	15·3	<u>0·16</u>	<u>0·87</u>	0·033	...	...
5	14·9	<u>0·85</u>	0·43	0·069	...	...
6	15·0	0·45	0·64	0·030	0·04	1·00
7	14·9	0·65	<u>3·70</u>	0·040	0·03	0·28
8	15·0	0·46	0·62	<u>0·60</u>	0·16	...
9	14·3	0·48	0·58	0·052	...	Mo. 3·50

\* The important variable element in each specimen is underlined.

### Experimental.

For the purposes of this investigation specimens were examined from alloys containing nominally 10% and 15% of silicon, respectively. All the alloys examined were of commercial purity and the materials used in their preparation were commercial ferro-silicon containing 75% of silicon, steel scrap, refined pig iron and commercial ferro-manganese, ferro-phosphorus, ferro-molybdenum and nickel. The chemical analyses of the specimens referred to are assembled in Table I.; the important variable element in each specimen is underlined.

The majority of the specimens were taken from material melted in a 25-cwt., three-phase, electric arc furnace. Specimens used for the investigation of special alloy additions were melted in a laboratory high-frequency furnace, and in each case both sand-cast and chill-cast specimens were prepared for examination under the microscope. Metallographic specimens were prepared by the usual methods and the etching reagent was a solution consisting of one part of nitric acid, one part of hydrofluoric acid and 6 parts of water. The effect of annealing on the microstructure was also investigated.

### *The Microstructure of High-Silicon Iron.*

The primary constituent in commercial high-silicon iron in the as-cast state, a typical example of which has the composition of

specimen 2, Table I., was the  $\alpha$  phase or silico-ferrite (Fig. 1). The carbon in the alloy was present, almost entirely, as graphite, which appeared under the microscope either as flakes, in varying degrees of coarseness, or in the finely divided form of the type frequently described as "supercooled graphite."

There appeared to exist a close relationship between the silicon content and the amount of carbon which could remain dissolved in the solid iron. In the case of high-carbon alloys, during solidification graphite rose to the surface of the molten metal in the form generally known as "kish." With lower carbon contents no graphite separation during the solidification period was observed.

The careful exploration of the specimens taken from commercial alloys revealed the presence of a second phase. This phase has been observed in small quantities in all commercial alloys containing from 10% to 15% of silicon in the as-cast condition. A typical example, taken from an iron having the composition of specimen 2, is shown in Fig. 2. In all cases this constituent, which has the appearance of cementite, was distributed apparently at random throughout the wall thickness of castings.

#### *The Effect of Annealing on the Stability of the Cementite-like Phase.*

It was found that the randomly distributed phase in the as-cast commercial 15% silicon iron disappeared on annealing at 800° C. A short annealing treatment of 1-2 hr. was sufficient to result in its complete breakdown to what appeared to be supercooled graphite and silico-ferrite, as shown in Fig. 3.

#### *The Effect of the Rate of Cooling from the Molten State on the Quantity and Distribution of the Cementite-like Phase.*

Rapid cooling through the solidification range caused an increase in quantity of the cementite-like phase. When castings of 10% silicon iron having the composition of specimen 1 were made in narrow metal moulds, the microstructure contained large amounts of the phase previously seen as traces only in castings slowly cooled in sand moulds. Graphite was absent from the outer skin of such chilled castings and the specimen had the microstructure shown in Fig. 4. In the interior of the specimen, where the rate of cooling was much less than at the outside, supercooled graphite and silico-ferrite were found.

With an iron containing as much as 15% of silicon (specimen 2) casting in a metal mould again decreased the amount of graphite in the surface zone of the specimen, and in its place the new phase appeared at the boundaries of the silico-ferrite. Considerable quantities of the boundary phase were produced, even in 15% silicon iron, when very rapid solidification was caused by pouring a thin stream of molten iron into cold water. Fig. 5 shows a micro-structure completely devoid of graphite, which was obtained when

specimen 2, containing 0.50% of carbon, was cast in the manner outlined here. The quicker the rate of cooling the greater was the tendency to produce the phase at the boundaries of the silico-ferrite crystals in all the irons examined.

*The Effect of Annealing on the Cementite-like Phase in Rapidly Cooled Samples of 10-15% Silicon-Iron.*

An annealing treatment of 1-2 hr. at 800° C., which was sufficient to cause the disappearance of the randomly distributed cementite-like phase in as-cast commercial silicon irons, was found also to result in the breakdown of the larger quantities of this phase which had been produced by rapid solidification in the manner described above. Since the products of decomposition were graphite and presumably silico-ferrite, there would seem to be little doubt that this phase, so readily stabilised by rapid cooling, was indeed a carbide phase. Attempts made to differentiate by acid-attack methods the silico-ferrite produced from the carbide on annealing were of no avail; its acid-resisting properties were of the same order as those of the silico-ferrite produced during initial solidification.

*The Effect of Various Elements on the Existence of the Carbide Phase. Carbon Content.*

In order to investigate the effect of varying carbon content on the ease of formation of the carbide phase, specimens 3, 4 and 5 were examined under the microscope in the water-quenched condition. The carbide phase was present in considerable quantities in all the specimens, although in specimen 3 (low carbon and specially low manganese and phosphorus contents) the phase was not so much in evidence as in the quenched specimen 4, which was made to contain a higher manganese content. This observation suggests that the presence of manganese and phosphorus cannot be overlooked in any explanation of the formation of this carbide phase. So far the authors have not yet been able to investigate the influence of very small percentages of manganese and phosphorus. From these experiments it would appear that the percentage of carbon in the 15% silicon iron had little effect upon the stability of the carbide, but the relative amounts of carbide and silico-ferrite visible under the microscope did vary with irons of different carbon content, as illustrated in Figs. 5, 6 and 7. Planimeter measurements showed that the ratio of carbide to ferrite bore a rough relationship to the amount of carbon in the alloy.

*Manganese.*

As was already indicated in the previous section, manganese had an important effect upon the stability of the carbide phase in 15% silicon iron. Manganese in amounts greater than 2% caused a marked increase in the residual carbide in a slowly cooled sand-cast



FIG. 1.—15% Silicon Iron; specimen 2. Sand-cast. Graphite and silico-ferrite.  $\times 120$ .



FIG. 2.—Same Specimen as in Fig. 1. Carbide phase, graphite and silico-ferrite.  $\times 600$ .

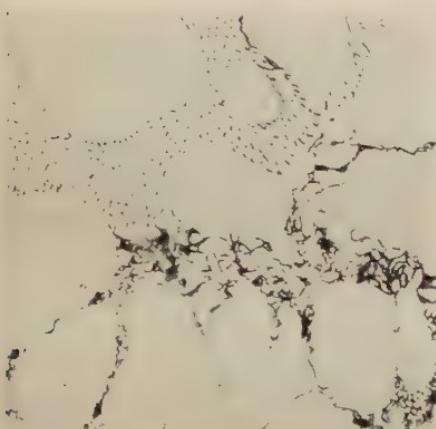


FIG. 3.—15% Silicon Iron; similar composition to specimen 2. Sand-cast and annealed at  $800^{\circ}$  C. for  $1\frac{1}{2}$  hr. "Fine graphite," fine flake graphite and silico-ferrite.  $\times 600$ .

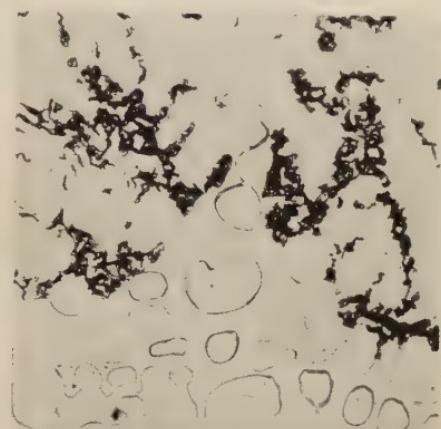


FIG. 4.—10% Silicon Iron; specimen 1. Chill-cast. Carbide, "fine graphite" and silico-ferrite.  $\times 600$ .  
Chilled surface

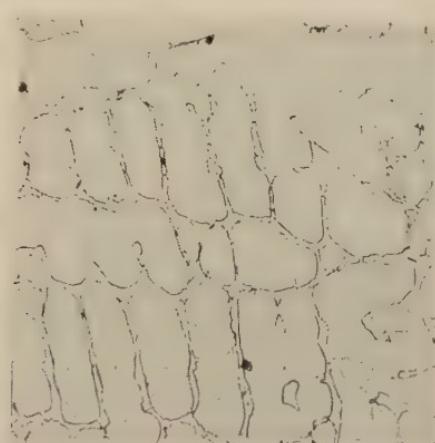


FIG. 5.—15% Silicon Iron, containing 0.50% of carbon; specimen 2. Water-quenched from molten state. Carbide and silico-ferrite.  $\times 600$ .

(Micrographs reduced to four-fifths linear in reproduction.)

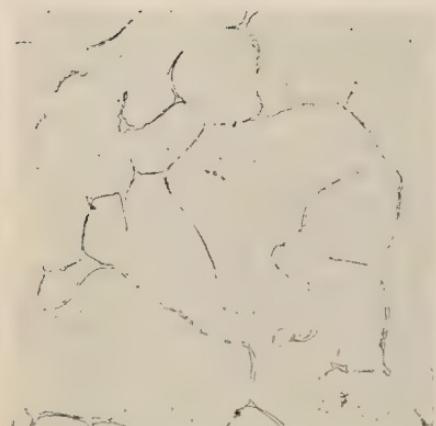


FIG. 6.—15% Silicon Iron, containing 0.16% of carbon; specimen 4. Water-quenched from molten state. Carbide and silico-ferrite.  $\times 600$ .

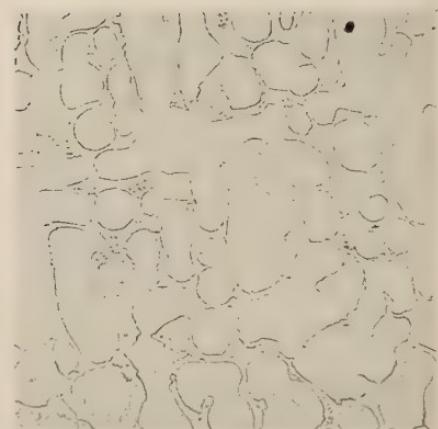


FIG. 7.—15% Silicon Iron, containing 0.85% of carbon; specimen 5. Water-quenched from molten state. Carbide and silico-ferrite.  $\times 600$ .



FIG. 8.—15% Silicon Iron, containing 3.7% of manganese; specimen 7. Sand-cast. Carbide, "fine graphite" and silico-ferrite.  $\times 600$ .



FIG. 9.—15% Silicon Iron, containing 0.60% of phosphorus; specimen 8. Sand-cast and annealed. "Fine-graphite," phosphide and silico-ferrite.  $\times 600$ .



FIG. 10.—15% Silicon Iron, containing 3.5% of molybdenum; specimen 9. Sand-cast. Complex carbide and silico-territe.  $\times 600$ .  
(Micrographs reduced to four-fifths linear in reproduction.)

silicon iron. Specimen 7, containing 14.9% of silicon and 3.7% of manganese, gave on slow cooling a microstructure in which approximately 50% of the total carbon was present as the carbide phase (Fig. 8). Water-quenching this alloy entirely eliminated the graphite. Annealing the water-quenched specimen at 800–900° C. decomposed the carbide phase.

#### *Phosphorus.*

Phosphorus in percentages over 0.1% in commercial 15% silicon iron was found to be a carbide stabiliser. Its action was to form a complex body which was apparently an intimate eutectic mixture of carbide and phosphide. This eutectic is readily visible in all commercial acid-resisting silicon irons containing upwards of 0.1% of phosphorus. Specimen 8 gave a carbide-phosphide eutectic of this type on slow-cooling in a sand mould. Annealing at 1050° C. for 4 hr. resulted in the breakdown of the carbide portions of the eutectic, and the phosphide only was left. Fig. 9 shows the remains of the carbide-phosphide complex after annealing, and the relatively large amount of carbide in the eutectic prior to annealing may be judged by the area of the resultant finely divided graphite.

#### *Molybdenum.*

Molybdenum, like phosphorus, stabilised the carbide in 15% silicon iron. Specimen 9, with 3½% of molybdenum, contained no free graphite, and had a microstructure, as shown in Fig. 10, reminiscent of a phosphoric 15% silicon iron.

#### *Nickel.*

Nickel, unlike the other elements discussed in this paper, had the effect of making the carbide phase less stable. No particles of residual carbide were detected in a sand-cast 15% silicon alloy having the composition of specimen 6. On water-quenching from the molten state, however, the nickel-bearing iron showed large areas of carbide when examined under the microscope, in the same way as with unalloyed silicon iron.

#### *Methods of Identification of Carbides.*

It is well known that cementite may be readily detected in steel by etching in boiling sodium picrate solution, whereupon blackening of this constituent takes place. The carbide in 15% silicon iron was not blackened by etching in the sodium picrate reagent. This was commented on previously by Kříž and Poboril (*loc. cit.*), who pointed out that perhaps the presence of silicon dissolved in the carbide phase might prevent it from acting in a normal manner towards sodium picrate solution.

That the carbide in 15% silicon iron decomposed to graphite on annealing was demonstrated in a simple way by chemical analysis. A water-quenched sample of specimen 2 was analysed before and

after annealing at 800° C. for 2 hr. The results given below are regarded as satisfactory proof that the phase under discussion is actually a carbide and that its decomposition products contain graphite :

*15% Silicon Iron.*

Total carbon after water-quenching . . . . .	0.50%
Graphitic carbon after water-quenching . . . . .	0.12%
Graphitic carbon after annealing . . . . .	0.47%

It was not possible to separate the carbide from a sample of 15% silicon iron, and, therefore, the exact composition of the phase could not be estimated chemically.

In quenched specimens containing the carbide phase and showing no graphite on careful examination under the microscope, it can be assumed that all the carbon in the alloy is contained in the carbide phase. On this assumption an attempt was made to determine its composition by planimetric measurements of the carbide and  $\alpha$ -phase areas in photomicrographs. Although the measurements depended to some extent upon the area of the specimen examined, the results were regarded as sufficiently accurate to establish that the phase did not have the composition of cementite. The average carbon content of the carbide phase in all the photomicrographs examined appeared to be between 2% and 3.5%. The carbon content of cementite,  $Fe_3C$ , is 6.6%. The possibility that the carbide may contain silicon is very strong, and if this were true it would not be expected to have the carbon concentration of cementite.

*Conclusions.*

It has been shown that a carbide phase can exist in alloys of carbon and iron containing as much as 15% of silicon. In small quantities this phase is present very often in commercial acid-resisting silicon-iron castings in the as-sand-cast condition. Its carbon concentration appears to lie between 2% and 3.5%.

Fine graphite of a type strongly resembling that described as "supercooled graphite" appears as a decomposition product on annealing specimens containing this carbide phase, and its stability is affected by alloying elements in a manner similar to their action on cementite in irons of lower silicon content.

The authors wish to thank Dr. W. G. Hiscock, Deputy Director-General Ordnance Factories (Explosives) to the Ministry of Supply, for permission to publish this paper.

*CORRESPONDENCE.*

Dr. F. R. MORRAL (Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., U.S.A.) wrote: This paper is interesting, since it calls attention to a new carbide. Have the authors tried to separate the carbide by a residue method and then examine the residue by X-ray diffraction?

In the Fe-Al-C system<sup>1</sup> a carbide phase was formed corresponding to  $\epsilon(\text{Fe}_3\text{Al})$ , containing approximately 4% of carbon. The metal atoms were analysed and found to consist of a face-centred lattice with 4 atoms in the unit cell. This phase has a different crystal structure from that of  $\text{Fe}_3\text{Al}$  in the Fe-Al system (body-centred cubic). In the Fe-Si system there is an  $\text{Fe}_3\text{Si}$  phase, also body-centred cubic. It would be interesting to determine whether the introduction of carbon into this system would produce a phase similar to that present in the Fe-Al-C system.

*AUTHORS' REPLY.*

The AUTHORS wrote in reply: We thank Dr. Morral for his contribution to the subject dealt with in our paper.

The possibility of the existence of some similarity between the carbides in the Fe-Si-C and Fe Al C systems is very interesting and might be well worth following up further.

We are not completely satisfied that the separation of carbides by residue methods is satisfactory. In the case of silicon-iron alloys containing round about 14% of silicon the corrosion resistance of the alloy is such as to make it extremely difficult to separate carbide by the usual methods involving electrolytic action or differential acid attack.

<sup>1</sup> F. R. Morral, *Journal of The Iron and Steel Institute*, 1934, No. II., p. 419.



# A NOTE ON THE MICROSTRUCTURE OF HIGH-SILICON ACID-RESISTING IRON.<sup>1</sup>

By J. E. HURST, D.MET., AND R. V. RILEY, B.Sc., Ph.D. (MESSRS. BRADLEY AND FOSTER, LTD., DARLASTON).

(Figs. 1 to 6 = Plates VI. and VII.)

## SUMMARY.

An unusual type of etched structure, referred to as the "barley shell" structure, has been described by various investigators of the iron-silicon alloys. The authors have observed it in their examination of commercial iron-silicon alloys containing upwards of 10% of silicon, and have recorded some conditions of etching under which it is obtained and some observations on its characteristics. It is readily obtained by etching with a reagent containing picric and hydrofluoric acids. It is not a true or real structure of the alloys, but its formation under the observed conditions is a characteristic of high-silicon iron alloys.

## INTRODUCTION.

In the metallographic examination of the alloys of iron and silicon several investigators from time to time have reported the occurrence of an unusual type of etched structure, particularly in the alloys of higher silicon content. Corson<sup>2</sup> appears to have been the first to observe "some fine but rather definite marks looking more or less like barley shells" during the examination of the microstructures of these alloys containing upwards of 6% of silicon. This same investigator more recently<sup>3</sup> described further examples of the occurrence of this "barley shell" structure in etched specimens of silicon iron containing from 5% to 14% of silicon. Some observations of the conditions under which this structure is produced were given, but no explanation of the phenomenon was attempted. The barley shell needles occurred in the iron-silicon alloys containing 5–14% of silicon and most frequently in the range 8–10% of silicon. They were particularly dense in a specimen quenched from 1000° C. The presence of carbon in the alloys tended to suppress the formation of the structure, but quenching of the carbon-containing alloy from 1000° C. had the opposite effect. The structure could not be eliminated by rubbing on a polishing wheel in the absence of abrasive.

Haughton and Becker<sup>4</sup> observed this same type of structure. They commented that it seemed to bear no relation to the constitution and that it was absent more often than otherwise. It

<sup>1</sup> Received June 21, 1943.

<sup>2</sup> *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1928, vol. 80, pp. 249–300.

<sup>3</sup> *Iron Age*, 1941, vol. 148, Aug. 28, pp. 45–49.

<sup>4</sup> *Journal of The Iron and Steel Institute*, 1930, No. I., p. 322.

appeared in a perfectly haphazard manner both in homogeneous and in duplex alloys, although very rarely in the latter, and it was suggested that it was probably a strain effect.

#### EXPERIMENTAL.

The barley shell structure has been observed frequently by the authors during the examination of commercial iron-silicon alloys containing from 10% to 15% of silicon, 0.10% to 0.60% of carbon, 0.30% to 0.70% of manganese and 0.05% to 0.20% of phosphorus. The structure was produced most readily by simple immersion, etching with a picric acid reagent consisting of 1 part of 5% picric acid in alcohol and 2 parts of hydrofluoric acid at room temperature for 15–30 sec. Deep etching with this reagent caused a thickening of the barley shell markings. Variations in the strength of the etching reagent and in the time of etching modified the appearance of the structure slightly.

The needles were found to be equally distributed both in the silico-ferrite and in the graphite areas. Under conditions of light etching the needles did not cross interdendritic holes in the specimen, but deeper etching caused a spread of the structure which eventually obscured small holes.

Corson's observation that a particularly dense barley shell structure was produced on a specimen which had been water-quenched from 1000° C. has not been confirmed, nor does the percentage of carbon in the alloy appear to affect the formation of this structure—an observation which is again contrary to that reported by Corson.

Commercial silicon-iron alloys of the above-mentioned composition consist essentially of a single metallic phase (silico-ferrite) together with graphite. The normal structure of the metallic phase is revealed by immersion-etching with a reagent containing 1 part of  $\text{HNO}_3$ , 1 part of HF and 6 parts of water for a period of 15–30 sec. at room temperature, and is illustrated in Fig. 1. The barley shell structure obtained by immersion-etching this same specimen with the picric acid reagent as detailed above is shown in Fig. 2.

With silicon contents in excess of 15.5% a second metallic phase appears; the true structure of these alloys obtained by immersion-etching with  $\text{HNO}_3 + \text{HF}$  reagent is reproduced in Fig. 3. The barley shell structure developed on this specimen by etching with the picric acid reagent is shown in Fig. 4.

Under light etching conditions the barley shell structure appears transparent, and under the microscope it is possible by altering the focus to observe either the barley shell needles or either of the normal structures occupying the same field, depending on the silicon content of the specimen.

Treatment of the specimens etched to show the barley shell structure with boiling water and organic solvents did not remove the structure; light rubbing on a dry cloth did not entirely efface



FIG. 1.—Silicon Iron, 14.8% of silicon. Normal structure of silico-ferrite and graphite. Etched with  $\text{HNO}_3 + \text{HF}$  reagent.  $\times 120$ .

[*Hurst and Riley.*  
To face p. 222 p.]



FIG. 2.—Same Specimen as Fig. 1. "Barley shell" structure. Etched with picric acid + HF reagent.  $\times 120$ .

(Micrographs reduced to four-fifths linear in reproduction.)



FIG. 3.—Silicon Iron, 16.1% of silicon. Normal two-phase matrix + graphite. Etched with  $\text{HNO}_3 + \text{HF}$  reagent.  $\times 600$ .

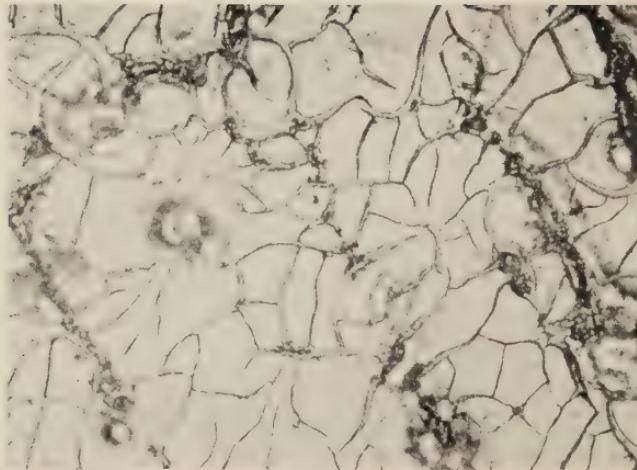


FIG. 6.—Same Specimen as Fig. 5, Experiment 10,  
"cracked film" structure, Etched with alcoholic  
 $\text{HNO}_3$  reagent.  $\times 600$ .

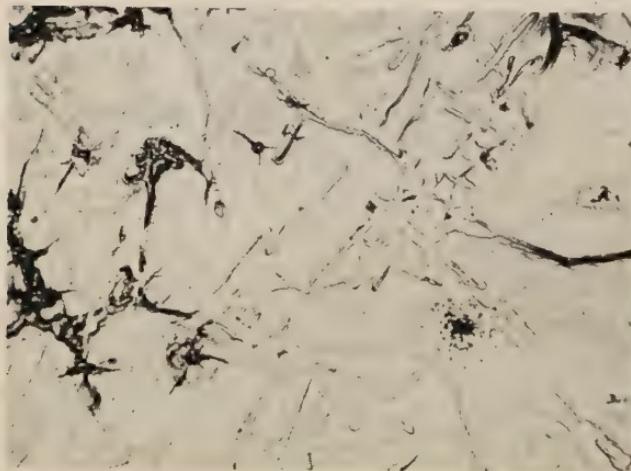


FIG. 5.—Silicon Iron, 15.6% of silicon. Experiment  
10. Etched with alcoholic  $\text{HNO}_3$  reagent.  $\times 600$ .

(Micrographs reduced to four-fifths linear in reproduction.)



FIG. 4.—Same Specimen as Fig. 3, "Barley shell"  
structure. Etched with picric acid + HF reagent.  
 $\times 600$ .

it, and after a deep etch the structure survived quite a violent rubbing on a dry cloth. These observations are sufficient to show that the structure cannot be regarded as merely a layer of crystals deposited from the etching solution.

After lightly polishing on a diamantine pad a specimen showing a dense barley shell structure, the tops of the individual needles appeared to have been ground away, leaving flat "plateaux" of micro-dimensions. Further polishing removed the needle structure completely, leaving a flat polished surface. The barley shell

TABLE I.—*Etching Results.*

Experiment No.	Etching Reagent.	Type of Etching Produced—	
		on Immersion.	on Electrolysis.
1	1 part 5% picric acid in alcohol : 2 parts HF.	"Barley shell" structure.	"Barley shell" structure.
2	1 part 5% picric acid in alcohol : 1 part HF : 6 parts alcohol.	Very faint "barley shell" structure.	"Barley shell" structure.
3	1 part acetic acid : 1 part HF : 1 part H <sub>2</sub> O.	No etching.	"Barley shell" structure.
4	4 parts acetic acid : 4 parts HF : 1 part HNO <sub>3</sub> .	"Barley shell" structure.	"Barley shell" structure.
5	1 part tartaric acid : 1 part HF : 2 parts H <sub>2</sub> O.	No etching.	"Barley shell" structure.
6	1 part tartaric acid : 1 part HNO <sub>3</sub> : 2 parts H <sub>2</sub> O.	No etching.	"Cracked film" structure.
7	Pure concentrated HNO <sub>3</sub> .	No etching.	"Cracked film" structure.
8	Pure concentrated HF.	"Normal" etching.	"Barley shell" structure.
9	1 part HNO <sub>3</sub> : 6 parts alcohol.	No etching.	No etching.
10	1 part HNO <sub>3</sub> : 3 parts alcohol : 3 parts H <sub>2</sub> O.	No etching.	"Cracked film" structure.
11	1 part HNO <sub>3</sub> : 1 part HF : 6 parts H <sub>2</sub> O.	"Normal" etching.	Faint "barley shell" structure.
12	1 part HNO <sub>3</sub> : 1 part HF : 1 part H <sub>2</sub> O.	Weak "barley shell" structure.	"Barley shell" structure.
13	1 part H <sub>2</sub> SO <sub>4</sub> : 4 parts H <sub>2</sub> O	"Normal" etching.	"Cracked film" structure.
14A	2 parts HF : 1 part 5% picric acid in alcohol; followed by—	"Barley shell" structure was dissolved away and "normal" etched structure remained.	...
14B	1 part HNO <sub>3</sub> : 1 part HF : 6 parts H <sub>2</sub> O.		

NOTES.—(1) In all cases of immersion and electrolysis the period of etching was from 10 to 30 sec. at room temperature.

(2) A "normal" etching is one showing areas of iron and graphite only with no trace of "barley shell" or "cracked film" structure.

(3) The reference to electrolysis implies that the specimen was made the anode in the liquid specified. A current at 8 V. was applied to the circuit.

structure could be erased completely by a careful second etch with the nitric-hydrofluoric acid reagent and the normal structure of silico-ferrite and graphite revealed.

The results of a number of experiments with different etching reagents and treatments are recorded in Table I. It was found that the barley shell structure could be produced by several etching reagents containing hydrofluoric acid either on immersion or on electrolysis. In the case of pure hydrofluoric acid itself, under conditions of immersion, "normal" etching was recorded and the barley shell structure was produced only on increasing the intensity of the attack of this reagent by electrolytic etching (Experiment 8). The nitric-hydrofluoric acid reagent in the concentration commonly used for the etching of high-silicon irons behaved in a similar manner, and with this reagent the barley shell structure could be obtained either by electrolytic etching or by increasing the acid concentration of the reagent (Experiments 11 and 12). The barley shell structure produced by the concentrated nitric-hydrofluoric acid reagent (Experiment 12) was obliterated and the normal structure developed by the dilution of this reagent with water; similarly in Experiment 14 the barley shell structure obtained by the picric-hydrofluoric acid reagent was removed and the normal structure revealed by a following etch with nitric-hydrofluoric acid reagent of the normal concentration as used in Experiment 11.

Certain etching reagents free from hydrofluoric acid produce structures which, although possibly different, under certain conditions may be confused with the true barley shell structure and like it do not represent the true phases present in the alloy. An example is given in Fig. 5, which shows the appearance of a specimen of 15% silicon iron electrolytically etched in a solution of 1 part of nitric acid, 3 parts of alcohol and 3 parts of water (Experiment 10). The same specimen more deeply etched by this same reagent exhibited a "cracked film" appearance, as illustrated in Fig. 6. In order to differentiate between this and the barley shell type of structure it is referred to in Table I. as the "cracked film" structure and its appearance with certain other reagents is recorded.

#### CONCLUSIONS.

The experimental observations recorded lead to the conclusion that the so-called "barley shell" and "cracked film" structures obtained under certain conditions of etching iron-silicon alloys of high silicon content are not the true structures of the alloys. Whilst the exact nature of these structures has not been determined experimentally, the authors' observations lead them to the view that they are both of film-like character and that their comparatively easy and rapid formation under the observed conditions is a characteristic of high-silicon iron alloys.

## CORRESPONDENCE.

Mr. C. B. SNODGRASS (Virginia Water, Surrey) wrote : The note by Dr. Hurst and Dr. Riley on the microstructure of high-silicon acid-resisting iron will be of great interest to those metallurgists who have studied closely the iron-silicon alloy system and attempted to elucidate the many problems associated with the production of acid-resisting cast iron.

The paper presents a certain amount of evidence which may lead to a better understanding of the barley-shell type of structure. The conditions under which the structure most readily forms appear to be associated with the presence of strong etching reagents, which probably attack the surface to no small degree, in spite of its acid-resisting nature, and there may be a strong tendency towards the formation of etching pits. Experiments 11 and 12 show that the barley-shell structure can be obtained by increasing the concentration of the reagent, or by electrolytic etching. The observation that light polishing on a diamantine pad removed a certain amount of the structure, while further polishing removed the structure entirely, seems to support the view that the structure is formed of numerous etching pits.

This theory that the barley-shell type of microstructure may be formed by a complicated system of etching pits is in accordance with the complex crystalline structure of high-silicon iron in the 10–15% range, and, indeed, satisfactory evidence of the point at which a second phase is introduced has not yet been obtained.

The apparently haphazard occurrence of the barley-shell needle-like structure in past literature may be accounted for by the fact that etching pits are often only obtained within a certain narrow range of conditions.

The fine interdendritic graphite structure shown in Fig. 1 is typical, but it is possible that the melting process and casting procedure may cause considerable modification to this. Have the authors considered to what extent a different mode of occurrence of the graphite would affect the formation of the needle-like structure? The ready formation of etching pits may be connected with the particular distribution of graphite.

While the authors deal chiefly with the commercial iron-silicon alloys, they mention that under the microscope it is possible to focus on the barley-shell needles or "either of the normal structures occupying the same field, depending on the silicon content of the specimen." Presumably only one normal structure is observed. It would, however, be of interest to know the range of silicon contents referred to in this statement.

The use of electrolytic etching for the examination of high-silicon iron appears to promote the formation of the needle-like structure. By varying the technique, have the authors been able to avoid the formation of this structure? The "cracked-film"

structure has not been observed by the writer, but it appears to be of a more film-like character than the barley-shell structure. However, it occurs only under electrolytic etching conditions and may, therefore, possibly be avoided by correct technique. A slight extension of the experiments given in the paper would, perhaps, enable the conditions to be established under which the normal structure can be obtained, as it should be the metallographer's aim to avoid the formation of misleading structures.

To summarise, the barley-shell structure may be a complicated etch-pit pattern, and this view provides an explanation for a number of observations made by the present investigators.

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#### AUTHORS' REPLY.

The AUTHORS wrote in reply : We wish to thank Mr. Snodgrass for his communication. In our opinion the barley-shell structure is a film, and we cannot agree that it is due to the formation of etching pits brought about by the use of strong reagents.

We agree that experiments 11 and 12 show that the barley-shell structure can be obtained by increasing the intensity of the etch, but this does not necessarily mean an increased tendency to etching pits. Whilst light polishing on a diamantine pad will erase the barley-shell structure, so also will a re-etch in a reagent composed of one part of nitric acid, one part of hydrofluoric acid and 6 parts of water (Experiment 14B, Table I.). Further evidence that the barley-shell structure is in no way connected with etching pits is afforded in Figs. 3 and 4, which show a normal and a barley-shell structure, respectively, in a two-phase iron-silicon alloy specimen. In Fig. 4 the "shells" cross over the two phases in an apparently haphazard manner, whereas had etching pits been responsible for the structure some difference in size or intensity of the markings would have been expected in the two regions.

As Mr. Snodgrass observes, changes in the graphite structure of commercial high-silicon acid-resisting iron can be brought about by variations in the melting procedure. Several types of graphite have been recognised in these alloys, ranging from a coarse flake type to a fine reticular variety, but the character of the barley-shell structure is quite independent of the form of the graphite.

The two normal structures to which reference is made in the seventh paragraph on the second page of the paper are structures showing the  $\alpha$  and the  $\alpha + \eta$  phases in Figs. 1 and 3, respectively. The second silicon-rich phase or  $\eta$  phase is normally found in commercial irons containing upwards of 15.3% of silicon.

The conditions of etching for the production of the normal structure with these acid-resisting irons are now well known and are specified in the fifth paragraph on the second page of the paper.

# THE APPARENT MICROSTRUCTURE PRODUCED BY HYDROFLUORIC ACID ETCHING REAGENTS ON PURE IRON AND IRON-SILICON ALLOYS.<sup>1</sup>

## “ BARLEY-SHELL ” MARKINGS.

BY DR. ING. W. J. WRAŻEJ (CAVENDISH LABORATORY, UNIVERSITY OF CAMBRIDGE).

(Figs. 1 to 12 = Plates VIII. and IX.)

### SUMMARY.

The investigation of the etching of iron-silicon alloys as well as pure (electrolytic) iron and also plain carbon steel and cast iron shows that, in all cases, when hydrofluoric acid is used as the etching reagent, the surface of the micro-samples is covered with scars (etch markings). Such scars, called “ barley-shell ” markings, appear when iron fluoride formed during the etching has the opportunity to crystallise (e.g., in the presence of alcohol or of alcoholic picric acid solution).

Other etching reagents such as mixtures of hydrofluoric acid and nitric acid in alcoholic or glycerol solution act in exactly the same way.

The crystal deposit formed during the etching is not removed when the samples are rinsed in alcohol. Washing the samples in water dissolves the crystal deposit and reveals the etching scars as the places where the crystals had been embedded. Thus, the scars have nothing in common either with the structure of the alloy or with its composition or condition. Examples are shown in the micrographs accompanying the paper.

When etching with hydrofluoric acid in alcoholic solution bivalent iron fluoride ( $\text{FeF}_2$ ) is produced, of which the space group is different from those shown in the literature. To investigate this point X-ray examinations and chemical analyses were made. The salts ( $\text{FeF}_2$ ) obtained from iron-silicon alloy and from electrolytic iron appear to have the same structure, which is hexagonal indexed on orthohexagonal axes. The true hexagonal unit cell dimension would be  $c = a = 9.645 \text{ \AA.}$ , the axial ratio being unity.

### INTRODUCTION.

DIFFERENT opinions have been expressed concerning the behaviour of iron-silicon alloys during etching by means of reagents containing hydrofluoric acid. Some fifteen years ago Corson<sup>2</sup> described the “ barley-shell ” markings as some sort of an unusual type of etched structure found in the iron alloys of higher silicon content. Corson

<sup>1</sup> Received December 16, 1943.

<sup>2</sup> M. G. Corson, *Transactions of the American Institute of Mining and Metallurgical Engineers*, 1928, vol. 80, p. 249.

gave no definite explanation, and since that time he and other investigators have referred to them without attempting any explanation of their formation,<sup>1, 2, 3</sup> except Hurst and Riley,<sup>4</sup> who pointed out the film-like character of the structure, which they said was characteristic of high-silicon iron alloys.

In Corson's opinion "some fine but rather definite marks looking more or less like barley shells" occurred in the iron-silicon alloys containing 5–14% of silicon and most frequently in the range 8–10% of silicon. Quenching the specimen from 1000° C. made the markings appear more dense. Rubbing on a polishing wheel without abrasive did not remove the structure.

Haughton and Becker<sup>1</sup> showed only one micrograph, calling the markings "oat seed," and said that "it is probably a strain effect."

Considering the different opinions expressed in the literature, the simple question arises whether the etching reagent producing the markings on an iron-silicon alloy can also produce similar markings on other iron specimens. If so, what is the cause? On the other hand, if the formation of these markings on an iron-silicon alloy is due to the presence of silicon in contact with the etching reagent, then it would not be expected on an ordinary iron specimen (plain carbon steel or electrolytic iron) during etching. There is the question, also, which component of the mixed etching reagent is responsible for the formation of these markings.

The answers to the questions were successfully worked out by using different investigational methods as described below.

## EXPERIMENTAL.

### *Micro-Examination.*

Throughout this investigation two etching reagents, mentioned below, were employed, because the aim was to discover the ultimate cause of the feature and not to experiment with etching reagents as such. They consisted of:

(1) 1 part hydrofluoric acid; 1 part nitric acid; 6 parts water.

(2) 1 part hydrofluoric acid; 1 part saturated solution of picric acid in alcohol.

These reagents as well as pure hydrofluoric acid were also used for dissolving either turnings from electrolytic iron or powder from the iron-silicon alloy. The solutions obtained in this way were crystallised for chemical, micrographic and X-ray examination.

<sup>1</sup> J. L. Haughton and M. L. Becker, *Journal of The Iron and Steel Institute*, 1930, No. I., p. 322.

<sup>2</sup> A. Osawa and T. Murata, *Nippon Kinzoku Gakkai-Si* (N.K.G.), 1940, vol. 4, Aug., No. 8, p. 228.

<sup>3</sup> M. G. Corson, *Iron Age*, 1941, vol. 148, Aug. 21, p. 45; Aug. 28, p. 45.

<sup>4</sup> J. E. Hurst and R. V. Riley, *Journal of The Iron and Steel Institute*, 1944, No. I., p. 221 P (this volume).

Using the etching reagents containing hydrofluoric acid, depending on circumstances the following features were noticed :

(a) When the samples were rinsed afterwards in alcohol the etched surfaces were covered with a deposit of small crystals (Fig. 1).

(b) After washing the etched surfaces with water they showed the existence of etch marks having the same forms as the previously existing crystals (Fig. 2). The same etch marks were seen when this crystal deposit was removed mechanically by scraping the surface with a celluloid strip (Figs. 3 and 4).

(c) The composition of the sample (iron-silicon alloy with about 15% of silicon, plain carbon steel, electrolytic iron and commonly used cast iron) had, as far as the present investigation shows, no influence. In all cases etching scars, so-called "barley-shell" markings, were produced when etching reagents suitable for producing them were used.

The bright places in Fig. 3 (iron-silicon specimen) and in Fig. 4 (electrolytic-iron specimen) show the barley-shell markings, because the deposit of salt was removed by scraping the surface with a celluloid strip.

The barley-shell markings have no connection with the structural components (*e.g.*, ferrite and pearlite in plain carbon steel); they cross the grain boundaries, and the etched sample rinsed in alcohol shows only the crystals, or, if the sample was washed in running water, the places (scars) where the crystals had been embedded. Fig. 5 illustrates a plain carbon steel etched with 4% picric acid. The normal ferrite and pearlite structure is present. Fig. 6 shows the same sample after additional etching in hydrofluoric acid + picric acid. The micrograph is focused to show the previously revealed structure and the salt crystals, which were produced at the surface during the secondary etching.

The mechanism of the formation of the barley-shell markings is as follows : The etching reagent containing hydrofluoric acid dissolves iron from the surface of the sample, forming a salt solution according to the chemical reaction  $\text{Fe} + 2\text{HF} = \text{FeF}_2 + \text{H}_2$ . In the presence of alcohol the iron fluoride crystallises as small crystals as is known and will be shown later on. On an etched surface the iron fluoride formed in the presence of alcohol crystallises in a regular manner. There is a close relation also between crystallisation and the progress of solution of iron atoms in hydrofluoric acid. The iron fluoride crystallises from the original nucleus and for further crystallisation the iron atoms which lie in the path of crystal growth are selected. In such a way it is clear how the shape of the scars (barley-shell markings) on the etched surface is produced.

The presence of organic liquids other than alcohol—*e.g.*, glycerol, used by Corson—will cause the same result. When the reagent consists of a mixture of other solvents besides hydrofluoric acid, *e.g.*,

nitric acid (reagent No. 1 with alcohol, and Corson's reagent), the salt formed will be the compound fluoride and nitrate of iron. It was to be expected also that the composition of the etched sample (*e.g.*, iron-silicon alloy or pure iron) would have some influence on the shape of the scars produced. There was in reality such a difference, because, for example, iron-silicon alloy is regarded as an acid-resisting iron and for that reason it showed more nicely developed barley-shell markings.

Short-time etching (a few seconds) produced only single scars, and they became more dense as the etching was prolonged. When hydrofluoric acid (without nitric acid—alcoholic reagent No. 2) was used the etching action ended when the whole surface of the sample was covered with crystals. Here, unlike reagent No. 1 with alcohol or Corson's reagent, prolongation of the etching time was without effect. When the etched sample was washed in running water so as to remove the remainder of the etching reagent, the subsequent etching produced new scars crossing those previously present.

Corson's reagent, consisting of 2 parts of hydrofluoric acid, 1 part of nitric acid and 2 parts of glycerol, behaved like reagent No. 1 containing alcohol. Both reagents were more active than hydrofluoric acid in alcohol or in an alcoholic saturated solution of picric acid (No. 2).

Fig. 7 represents the electrolytic-iron sample etched for 5 sec. Some of the single bunch-like etch markings cross the grain boundaries, which proves that they have nothing in common with the structure of the sample. The same sample after being etched a second time showed the background deeply attacked by the reagent. Different shapes of scars could be recognised, *e.g.*, "brushes," stars, single marks, &c. Fig. 8 shows one of the places with a deeply etched background and some single barley-shell markings.

Corson's reagent when used for etching the commercial iron-silicon alloy sample (14.9% of silicon) behaved similarly, *i.e.*, acted very rapidly. As the alloy contained silicon the appearance of the etching scars was altered. Fig. 9 shows the sample etched for 20 sec. Some of the etching marks cross the grain boundaries, which again proves that the etching scars bear no relation to the structure of the iron-silicon alloy. A subsequent etching for 20 sec. produced new but deep and dense scars, as can be seen in Fig. 10. These barley-shell markings could disappear entirely after subsequent longer etching and the background became blurred, although new marks could be found on such a deeply etched background (*e.g.*, see Fig. 8).

#### X-Ray Examination.

From the micro-examination the question arose what is the atomic structure of the crystals forming the deposit on the surface of an etched sample? Also, have the crystals on an electrolytic-iron sample the same atomic structure as those on an iron-silicon alloy?

The crystal deposits on both samples were examined on the

samples themselves by the low-angle glancing reflection method of X-ray examination. The scrapings from the surfaces of the specimens as well as the salts produced from both the samples, crystallised on cellophane, were examined by the X-ray powder method.

It was noticed that reagent No. 2 gave a thinner deposit of salt on the etched surface than pure hydrofluoric acid + alcohol or reagent No. 1 with alcohol; the last-named gave a thick deposit of salt. The electrolytic iron was more easily attacked by the reagent than the iron-silicon alloy.

Although the salt deposit on the iron-silicon alloys was easily detected under the microscope (see Fig. 3) and by the X-ray low-angle glancing reflection method, it was not obtained in an amount sufficient for examination by the X-ray powder method.

Besides the salt from the deposits, salts were produced from turnings of the electrolytic iron and from the powdered pure iron-silicon alloy (*S.E. 15*, National Physical Laboratory, containing 15% of silicon) by dissolving them in pure hydrofluoric acid or the above-mentioned reagents; the solutions so obtained were crystallised on film for micrographic study and on cellophane for examination by the X-ray powder method.

*The X-ray powder method* photographs were taken from :

- (a) Deposit scraped from the polished surface of the electrolytic-iron specimen etched with hydrofluoric acid + alcohol (film No. 3987).
- (b) Salt obtained from electrolytic iron dissolved in pure hydrofluoric acid (films Nos. 3993, 4183).
- (c) Salt obtained when the solution prepared as in (b) was treated with a large amount of alcohol (film No. 4147).
- (d) Deposit scraped from the polished surface of commercial iron-silicon alloy etched with hydrofluoric acid + alcohol (film No. 4029).
- (e) Salt obtained from pure iron-silicon alloy dissolved in pure hydrofluoric acid (film No. 4028).
- (f) Salt obtained when the solution prepared as in (e) was treated with a large amount of alcohol (film No. 4154).
- (g) Salt obtained from electrolytic iron dissolved in hydrofluoric acid + picric acid + 10% of water (film No. 4033).
- (h) Salt obtained from pure iron-silicon alloy dissolved in hydrofluoric acid + picric acid + 10% of water (film No. 4041).

All the films mentioned above, taken in a 19-cm. Debye-Scherrer camera, as well as many others not mentioned and many taken in a 9-cm. van Arkel camera, gave the same pattern of structure with spacing  $d$  as shown in Table I. Comparison of the spacing data shows that the X-ray powder photographs are identical. In other words, in all cases, independent of the kind of sample used (iron-silicon alloy or electrolytic iron), the hydrofluoric acid reagent produces the same kind of salt.

TABLE I.—*Spacing Data from the X-Ray Powder Photographs. Hydrofluoric Acid Etching Reagent.*All films taken with Fe  $K_{\alpha}$  radiation except No. 4041 (Co  $K_{\alpha}$ ).

Intensity.*	Film Nos.									Average.
	3987.	3993.	4028.	4029.†	4033.	4041.	4147.	4154.	4183.‡	
V.s.	4.82	4.83	4.81	4.83	4.81	4.81	4.83	4.81	4.81 <sub>45</sub>	4.81 <sub>3</sub>
S.	4.18	4.19	4.19	4.19	4.19	4.19	4.19	4.19	4.18 <sub>39</sub>	4.18 <sub>3</sub>
W..	3.81	3.82	...	3.82	3.80	3.80	3.80	3.82	3.81 <sub>72</sub>	3.81 <sub>1</sub>
S..	2.64	2.64	2.64	2.64	2.64	2.64	2.64	2.63	2.63 <sub>69</sub>	2.63 <sub>8</sub>
M.s.	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24 <sub>41</sub>	2.24
M..	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91 <sub>55</sub>	1.91
M..	1.87	1.86	1.87	...	1.87	1.87	1.87	1.87	1.87 <sub>39</sub>	1.86 <sub>9</sub>
M..	1.81	1.81	1.82	...	1.82	1.81	1.81	1.81	1.81 <sub>15</sub>	1.81 <sub>2</sub>
M..	1.77	1.77	1.77	...	1.77	1.77	1.77	1.77	1.77 <sub>47</sub>	1.77
M.s.	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66	1.66 <sub>84</sub>	1.66 <sub>1</sub>
M.w.	1.60	1.60	1.60	...	1.60	1.60	1.60	1.60	1.60 <sub>62</sub>	1.60 <sub>1</sub>
W..	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57 <sub>53</sub>	1.57
W..	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49	1.49 <sub>41</sub>	1.49
M.w.	1.38	1.38	1.39	...	1.39	1.39	1.39	1.39	1.38 <sub>96</sub>	1.38 <sub>8</sub>
M..	1.33	1.33	1.33	...	1.33	1.33	1.33	1.33	1.33 <sub>48</sub>	1.33
M.s.	1.22	1.22	1.22	...	1.23	1.23	1.23	1.23	1.22 <sub>73</sub>	1.22 <sub>4</sub>
W..	1.15	1.15	1.15	...	1.15	1.15	1.15	1.15	1.15 <sub>43</sub>	1.15
W..	1.10	1.10	...	...	1.10	1.10	1.10	1.10	1.10 <sub>23</sub>	1.10

\* V.s. = very strong. S. = strong. M.s. = medium strong. M. = medium. M.w. = medium weak. W. = weak.

† The film was very weak, owing to the use of a rather thick manganese filter.

‡ The third and fourth decimal places are shown in order to indicate approximately that some changes are to be expected. The exact data will be obtained from single crystals.

It is striking that in the case of iron-silicon alloy the silicon present does not alter the crystalline structure of the salt. With the commercial cast also the presence of graphite, although it changes the colour of the salt deposit scraped from the etched surface from white to grey, does not change the atomic structure of the salt.

The spacing data from X-ray powder photographs (films No. 4000, deposit, and No. 4004, salt), when a mixture of hydrofluoric acid and nitric acid had been used, are shown in Table II. Only

TABLE II.—*Spacing Data from X-Ray Powder Photographs. Mixed Hydrofluoric-Nitric Acid Etching Reagent.*Films taken with Fe  $K_{\alpha}$  radiation.

Intensity. (As in Table I.)	Film No. 4004.	Film No. 4000.	Average from Table I.	Intensity. (As in Table I.)	Film No. 4004.	Film No. 4000.	Average from Table I.
V.s.	4.86	...	...	S..	1.92	1.91	1.91 (m.)
M.s.	...	4.81	4.81 <sub>8</sub> (v.s.)	W..	1.90	...	1.86 <sub>9</sub> (m.)
S..	4.60	4.56	...	M.w.	1.83	...	1.81 <sub>2</sub> (m.)
S..	4.31	4.29	...	W..	1.78	...	1.77 (m.)
S..	4.20	4.17	4.18 <sub>8</sub>	M.s.	1.67	1.66	1.66 <sub>1</sub>
W..	3.85	3.84	3.81 <sub>1</sub>	W..	1.58	...	1.57
W..	3.25	3.23	...	M.w.	1.39	1.39	1.38 <sub>6</sub>
S..	2.65	2.64	2.63 <sub>8</sub>	V.w..	...	1.33	1.33 (m.)
S..	2.26	2.24	2.24 (m.s.).	V.w..	1.23	...	1.22 <sub>4</sub> (m.s.)

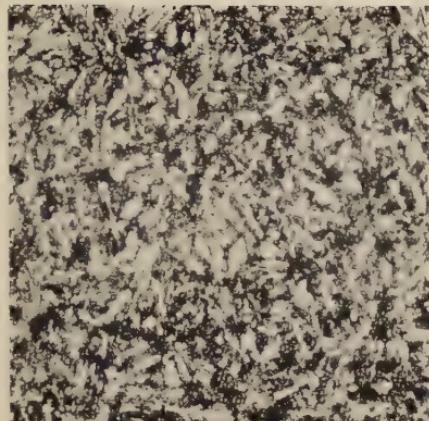


FIG. 1.—Rinsed in alcohol. Crystals difficult to focus.  $\times 240$ .

FIGS. 1 and 2.—Iron-Silicon Alloy (15-75% Si), etched in HF + picric acid and rinsed.



FIG. 2.—Rinsed in water. Etch marks show sites of crystals.  $\times 250$ .



FIG. 3.—Commercial iron-silicon alloy.  $\times 240$ .

FIGS. 3 and 4.—Deposits of Small Crystals, after etching in HF + picric acid. Bright areas scraped to show etch marks.



FIG. 4.—Electrolytic-iron specimen.  $\times 200$ .



FIG. 5.—Primary etch, normal structure of ferrite and pearlite.  $\times 250$ .

FIGS. 5 and 6.—Plain Carbon Steel, etched first in 4% picric acid.



FIG. 6.—Structure affected by etch marks produced by secondary etch in HF + picric acid.  $\times 500$ .

[*Wragej.*  
[To face p. 232 p.]



FIG. 7.—First etching for 5 sec. Some etch marks cross grain boundaries.  $\times 600$ .

Figs. 7 and 8.—Electrolytic Iron, etched in Corson's reagent.



FIG. 8.—Second etching. Although background deeply attacked, new marks are visible.  $\times 600$ .



FIG. 9.—First etching for 20 sec. Some etch marks cross grain boundaries.  $\times 600$ .

Figs. 9 and 10.—Commercial Iron-Silicon Alloy (14.9% Si), etched in Corson's reagent.



FIG. 10.—Second etching for 20 sec. Etch marks very deep and dense.  $\times 600$ .

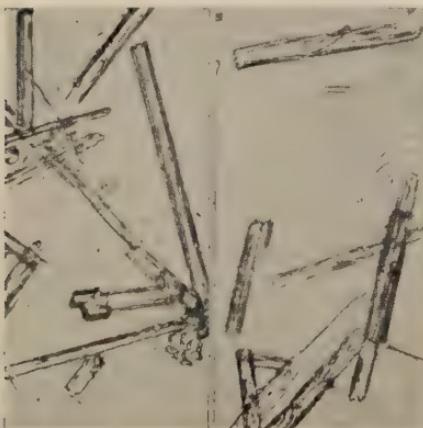


FIG. 11.—From electrolytic iron.  $\times 240$ .

Figs. 11 and 12.— $\text{FeF}_2$  Needles (transmitted light); metal dissolved in HF, and alcohol added to solution.



FIG. 12.—From iron-silicon alloy.  $\times 240$ .

[Wrazej.  
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some strong lines on the X-ray photograph coincide with the above-described pattern. This proves that the salts were of different crystalline structure, although the scars were very similar to the above-mentioned markings produced when the hydrofluoric acid reagent was used.

The low-angle glancing reflection method was used for the surface examination of specimens before and after etching; specimens of electrolytic iron and of commercial casts with 14.9% and with 15.75% of silicon were examined. In all cases the specimen was oscillated through 5° during the exposure, being inclined at 5–10° to the X-ray beam.

The samples were examined both microscopically and by means of X-rays in the following conditions : (a) After polishing (*i.e.*, unetched); (b) after etching in hydrofluoric acid + picric acid, rinsing in alcohol and drying in a current of air; and (c) after etching, rinsing in running water and drying in a current of air.

In all cases, for calculation, two photographs were taken, one with the film near the sample and the other 3 cm. further away.

The results of the examination were as follows :

In condition (a) the samples showed very pronounced iron lines on the film, of which the position was in perfect accordance with the lattice parameter of the sample examined (*i.e.*, iron-silicon alloy or electrolytic iron).

In condition (b) the samples showed new and very pronounced lines of the salt deposit always at the same angles of reflection, and calculation of the reflecting plane distances obtained gave results identical with the strong lines ( $d = 4.81$  and  $4.19 \text{ \AA}$ ) obtained by the powder method. A micrograph of the salt deposit (commercial iron-silicon alloy) is shown in Fig. 1.

In condition (c) the surfaces etched and rinsed in water gave identically the same lines as in condition (a), *i.e.*, no other lines except those due to iron were detected. All samples in this case showed very pronounced etching scars, as seen in Fig. 2, representing a commercial iron-silicon alloy (15.75% of silicon).

The low-angle glancing reflection method must be considered to be very sensitive, because any residue of the salt deposit left after inadequate washing of the sample in water was easily detected during X-ray examination. The lines of the traces of salt deposit were very distinct.

That the  $\text{FeF}_2$  salt would be present when iron samples were etched with hydrofluoric acid reagent or when iron was dissolved in hydrofluoric acid was obvious, and one would expect that when the X-ray photographs were taken by one of the two above-mentioned methods they would be easily identified. This was not the case. A search was made through the chemical literature and tables of

structure,<sup>1</sup> but without result. It was decided to obtain a single crystal and to determine the real data for this salt. The question was simply this: Since the lines could not be identified by means of the data given in the literature, either the determination or the space group recorded there was not accurate or the material ( $\text{FeF}_2$ ) examined was different. The first assumption was more likely.

Preliminary measurements on single-crystal photographs showed that, if the crystal was tetragonal, its space group could not be  $D_{4h}^{14}$ , since  $(hkl)$  is present in all orders as well as  $(hk0)$  and  $(0kl)$ . In any case, the  $\text{FeF}_2$  salt is not tetragonal, because the intensities of reflection from the planes  $hkl$  and  $k\bar{h}l$  are quite different. In spite of the fact that they should occur at the same angle, it was almost always found that if  $hkl$  was present  $k\bar{h}l$  was absent, and vice versa.

For the single-crystal investigation the minute crystal, obtained as described below, was rotated through  $360^\circ$ ; it was also oscillated through  $15^\circ$  about the assumed principal axes, being turned through  $13^\circ$  between each set of oscillations, in order that the photographs should overlap. This examination led to the values  $a = b = 9.64 \pm 0.025 \text{ \AA.}$ , and  $c = 16.79 \pm 0.10 \text{ \AA.}$  These data are only approximate and will be determined more accurately later.

Although the unit cell, as given above, is rectangular with  $a$  equal to  $b$ , this is a pure coincidence—compare the case of gallium (Laves<sup>2</sup> and Bradley<sup>3</sup>), which was proved to be orthorhombic in spite of the fact that two axes were approximately equal.

In the present instance the further coincidence is observed that  $c = \sqrt{3}a$ . This suggests that the structure is hexagonal indexed on orthohexagonal axes. The true hexagonal unit cell dimensions would be  $c = a = 9.645 \text{ \AA.}$ , the axial ratio being unity. This solution is now being tested in collaboration with Dr. A. J. Bradley.

### *Chemical Investigation.*

The mixture of hydrofluoric acid and alcohol and the solution of hydrofluoric acid and saturated picric acid in alcohol must be regarded in this case as equivalent, because both produce the same feature on the polished samples of iron-silicon alloy or pure electrolytic iron.

<sup>1</sup> "Gmelins Handbuch der anorganischen Chemie," 8th edition, "Eisen," Teil B, Lieferung 1, pp. 174–175 (Berlin, 1929: Verlag Chemie, G.m.b.H.), gives the following data:

$\text{FeF}_2$ ,  $D_{4h}^{14}$  type:  $a = 4.83 \pm 6 \text{ \AA.}$ ,  $c = 3.36 \pm 6 \text{ \AA.}$ ,  $c/a = 0.69$  (V. M. Goldschmidt);  $a = 4.670 \pm 5 \text{ \AA.}$ ,  $c = 3.297 \text{ \AA.}$ ,  $c/a = 0.706$  (A. Ferrari).

"Handbook of Chemistry and Physics," 23rd edition, p. 1603 (Cleveland, Ohio, 1939: Chemical Rubber Publishing Co.), gives the following data:

$\text{FeF}_2$ ,  $D_{4h}^{14}$  type ( $\text{SnO}_2$ ):  $a = 4.670 \text{ \AA.}$ ,  $c = 3.297 \text{ \AA.}$

<sup>2</sup> Laves, *Zeitschrift für Kristallographie*, 1933, vol. 84, p. 256.

<sup>3</sup> A. J. Bradley, *Zeitschrift für Kristallographie*, 1935, vol. 91, p. 302.

In using the well-known sensitive properties of solutions of potassium thiocyanate, KCNS, and potassium ferricyanide,  $K_3(Fe(CN)_6)$ , in determining the valency of the salts, the surfaces of the samples were examined after etching, both with the salt deposit and without it.

In no case did KCNS solution produce a blood-red or even amber colour on freshly etched samples covered with salt deposit. The characteristic bluish colour was obtained when  $K_3(Fe(CN)_6)$  solution was applied. The samples etched and rinsed in water, *i.e.*, without salt deposit, of course, gave no reaction with the solutions.

From the above chemical tests as well as from the references in the chemical literature it may be concluded that the crystal deposit consists of ferrous fluoride ( $FeF_2$ ).

To obtain the salt ( $FeF_2$ ) pure iron-silicon alloy (15% silicon) or electrolytic iron was dissolved in hydrofluoric acid in a platinum crucible (a celluloid crucible could equally well be used). The crucible was filled nearly full and covered during solution, so that only a small space was left; the atmosphere in that space, to some extent replacing the air, consisted of hydrogen liberated during the reaction and the vapour of hydrofluoric acid.

The salt obtained when the solution was treated with alcohol consisted of very minute needles, shown in Fig. 11 (from electrolytic iron) and Fig. 12 (from iron-silicon alloy).

Such needles when tested with solutions of KCNS and of  $K_3(Fe(CN)_6$ ) gave only the reaction for bivalent iron. When the salt was kept for several days it underwent some change, *i.e.*, showed traces of tervalent iron. The reaction with KCNS was positive (amber or even red). The  $K_3(Fe(CN)_6$ ) reaction remained still dominant. The samples with salt deposits behaved in the same way, and need no further comment.

The crystals for single-crystal X-ray examination were obtained from the liquid kept in a cellophane container. The liquid was protected from oxidation, so as to prevent the formation of tervalent iron. Satisfactory single crystals were prepared by placing some of the solution on a photographic plate previously fixed in "hypo," well washed and dried; the dry emulsion absorbed the water from the liquid and the concentrated solution crystallised quickly, giving nicely shaped crystals, which could be examined in polarised light without removal from the plate.

The single crystals were kept in alcohol; in that state some crystals were selected under the microscope for single-crystal X-ray examination, while others were crushed and checked up by the X-ray powder method. The latter examination confirmed that the salt deposit scraped from the samples, the salt from solutions treated with alcohol and also the single crystals were all of the same chemical composition and crystallographic structure.

The specific gravities of the salts obtained when the solution was treated with alcohol and of the single crystals were determined, using

heavy liquids. The specific gravity of the salt from electrolytic iron differed somewhat from that of the salt prepared from iron-silicon alloy; the values were 1.96 and 1.97, respectively. The specific gravities were determined by Dr. F. Coles Phillips in Professor C. E. Tilley's Department of Mineralogy and Petrology, University of Cambridge.

#### ACKNOWLEDGMENTS.

The author wishes to thank Professor Sir Lawrence Bragg, F.R.S., for his interest in this work and his encouragement as well as his extremely valuable advice. Thanks are also due to Dr. A. J. Bradley, F.R.S., Dr. H. Lipson and Dr. A. J. C. Wilson for their kind assistance in the X-ray investigation. The author has also to express his best thanks to Dr. J. E. Hurst for suggesting this interesting problem to be treated in Professor Bragg's laboratory, which demanded the use of various X-ray methods.

The author also wishes to acknowledge the generous assistance rendered by the Commander of the Institute of Technical Research, General Staff, Polish Army, Colonel Stanislaw Witkowski, Dipl. Ing., and finally that of Emmanuel College in providing him with home-like accommodation during his year's stay in Cambridge, enabling him to carry out this investigation and to complete other work as well.

#### CORRESPONDENCE.

Dr. U. R. EVANS (Cambridge University) and Dr. A. W. CHAPMAN (Sheffield University) wrote: Dr. Wrażej is to be congratulated on having shown that silicon is not needed for the somewhat mysterious barley-shell markings, which he has obtained on electrolytic iron free from silicon. Since the results suggest that the markings are due to a layer of ferrous fluoride, it may be of interest to recall some other evidence of the formation of fluoride films on iron.

Early work on corrosion at Cambridge<sup>1</sup> showed that solutions of potassium or sodium salts containing oxygen corrode iron rapidly in those cases where the corresponding iron salt is soluble; thus, potassium or sodium chloride cause marked attack on iron. On the other hand, in cases where the iron salt is sparingly soluble, the iron remains bright and unattacked in a solution of the sodium or potassium salt; thus, sodium phosphate solution has no action on iron in the presence of water. In 1930 experiments were extended to potassium fluoride solutions at Sheffield,<sup>2</sup> when it was found that fluorides behave like chlorides at low concentrations, but more like phosphates at high concentrations. In dilute solution, the attack

<sup>1</sup> U. R. Evans, *Journal of the Society of Chemical Industry*, 1925, vol. 44, p. 163 T; 1927, vol. 46, p. 347 T. *Journal of the Chemical Society*, 1929, p. 111.

<sup>2</sup> A. W. Chapman, *Journal of the Chemical Society*, 1930, p. 1546.

by potassium fluoride solution was almost the same as that by potassium chloride solution, but above 0·8*N* the attack by fluoride solution suddenly fell off to a very low value. This was attributed to a film consisting of fluoride (or double fluoride) of iron, and the fact that inhibition of corrosion occurred only at high concentrations of fluoride can be explained when it is remembered that, owing to the common ion effect, ferrous fluoride will be much less soluble in concentrated potassium fluoride solution than in a dilute solution of the same salt.

Other cases are known where a salt is corrosive at low concentrations and inhibitive at high concentrations. A dilute solution of sodium bicarbonate rusts iron very rapidly, but in contact with a concentrated solution iron remains bright and passive.

In the work at Sheffield mentioned above evidence was obtained that the protective film produced by potassium fluoride might be a double potassium ferrous fluoride. The fact that the X-ray data obtained by the author in respect of the deposit formed by hydrofluoric acid differ from those for known forms of ferrous fluoride suggests that the deposit might perhaps be an acid salt or a double salt rather than normal  $\text{FeF}_2$ . It would be interesting to know whether these possibilities can be definitely excluded.

If it is desired to use etching or pickling agents containing hydrofluoric acid (and these appear to be necessary in etching high-silicon irons, and to be convenient in pickling certain stainless steels), and yet to avoid the production of a film on the surface, it will be necessary to work out concentrations which do not cause the solubility product of ferrous fluoride to be exceeded. The avoidance of solid fluoride layers may be important both in metallographic work and in industrial pickling. In metallography, the appearance of these markings may lead observers to think that an alloy which is really homogeneous contains more than one phase, whilst, in pickling, the irregular corrosion associated with deposits may presumably increase the expense and trouble of obtaining the desired surface finish.

The author writes that "there is also a close relation between crystallisation and the progress of solution of iron atoms in hydrofluoric acid. The iron fluoride crystallises from the original nucleus, and for further crystallisation the iron atoms which lie in the path of crystal growth are selected." This seems to suggest that the proximity of a growing fluoride crystal causes adjacent iron atoms in the metal to be selected for solution. If that is the author's meaning, two explanations suggest themselves. The concentration of iron ions near a growing crystal will probably be less than elsewhere, since there will be no supersaturation, and consequently the potential will be shifted in the anodic direction at such points. The alternative suggestion is that many cases are known where attack occurs preferentially at the junction of three phases, perhaps owing to the general loosening of the structure at such junctions.

Dr. H. LIPSON (Crystallographic Laboratory, University of Cambridge) wrote : Dr. Wrażej's determination of the symmetry of his crystal cannot be considered as final. He claims that although his crystals have a pseudo-tetragonal unit cell they are really hexagonal. In this case the indexing on orthohexagonal axes should show absences of the spectra with  $h + k$  odd ; yet it is claimed that there are no such general absences. The only explanation of these results is that the crystals are really orthorhombic with axial ratios of unity and  $\sqrt{3}$ . This is a surprising set of coincidences, but it is not, of course, impossible.

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*AUTHOR'S REPLY.*

Dr. WRAZEJ wrote in reply : I am very pleased to learn so much from Dr. Evans and Dr. Chapman's contribution, and entirely agree with all that they say. I appreciate their remarks about the cases where attack occurs preferentially at the junction of three phases, owing to the general loosening of the structure at such a junction.

It had been my intention to investigate only the mechanism of the formation of barley-shell markings ; hence I have not carried my chemical researches further. For that reason I am indebted to Dr. Evans and Dr. Chapman for their contribution, which goes a long way towards completing my findings.

I read Dr. Lipson's comments with great interest, for they suggest a structure other than that found by myself. This point will be re-examined with great care during the further work on the crystal structure which still remains to be done.

# THE EFFECT ON THE HARDENABILITY OF SMALL ADDITIONS OF CHROMIUM AND MOLYBDENUM TO A GRAIN-SIZE-CON- TROLLED 0·9% NICKEL STEEL.\*

By W. STEVEN, Ph.D., A.R.T.C. (RESEARCH DEPARTMENT, MESSRS.  
WILLIAM JESSOP & SONS, LTD., SHEFFIELD).

(Under the direction of Mr. D. A. Oliver, M.Sc., F.Inst.P.)

## ABSTRACT.

Nineteen grain-size-controlled steels (American Society for Testing Materials grain size  $6\frac{1}{2} \pm 1$ ) of the following foundation analysis (by weight) were made by the crucible process: Carbon  $0\cdot33 \pm 0\cdot04\%$ ; manganese  $0\cdot60 \pm 0\cdot10\%$ ; silicon  $0\cdot21 \pm 0\cdot04\%$ ; sulphur  $0\cdot039 \pm 0\cdot007\%$ ; phosphorus  $0\cdot020 \pm 0\cdot004\%$ ; and nickel  $0\cdot89 \pm 0\cdot03\%$ .

The effect of simultaneous additions of molybdenum and chromium to this steel over the range zero to  $0\cdot6\%$  of molybdenum and  $0\cdot2\%$  to  $0\cdot8\%$  of chromium was determined by the Jominy end-quench method. The results indicate that the hardenability of these steels does not vary as the quenching temperature is altered from  $850^\circ$  C. to  $880^\circ$  C. or as the time of soaking at the quenching temperature is increased from 20 minutes to 60 minutes.

When the hardenability of this series of steels is expressed in terms of Grossmann's ideal critical diameter ( $D_\infty$  inch) the following relation exists between the hardenability and the weight percentages of chromium and molybdenum :

$$D_\infty = 2\cdot36 \text{ Cr}^2\text{Mo} + 2\cdot00 \text{ CrMo} + 0\cdot60 \text{ Mo} + 1\cdot70 \text{ Cr} + 1\cdot31.$$

This equation enables the hardenability of any steel within the range of analysis investigated to be calculated from its chemical composition. Ideal critical diameters calculated from analysis figures by Grossmann's method agree only approximately with the experimental results.

By using the above equation, data are tabulated indicating the percentages of chromium and molybdenum required to produce a steel of a given ideal critical diameter, and three iso-hardenability diagrams have been drawn giving the critical diameters corresponding to an ideal quench, a water-quench and an oil-quench.

THE object of this investigation was to study by means of the Jominy test the variation in the hardenability of a grain-size-controlled 0·9% nickel steel as the chromium content varied from 0·2% to 0·9% and as the molybdenum content varied from zero to 0·6%, keeping the grain size as nearly as possible constant.

### *(1) Production and Analysis of Steels Tested.*

The steels tested were made by the crucible process in fireclay pots from ingot iron and standard alloying materials. The melts,

\* Received August 9, 1943.

which weighed approximately 60 lb. each, were cast into 3-in. ingots, and the grain was controlled by a total mould addition of 0.5 oz. of aluminium. The ingots were rolled to 1½-in. dia. bar. This corresponds to a reduction of slightly more than 7 to 1.

The foundation analyses of the steels investigated lie within the following specification :

Carbon . . . .	$0.33 \pm 0.04\%$	Sulphur . . . .	$0.039 \pm 0.007\%$
Manganese . . . .	$0.60 \pm 0.10\%$	Phosphorus . . . .	$0.020 \pm 0.004\%$
Silicon . . . .	$0.21 \pm 0.04\%$	Nickel . . . .	$0.89 \pm 0.03\%$

by weight,

which is represented by steel No. 1. The remaining steels fall into four series containing in addition  $0.20 \pm 0.01\%$ ,  $0.44 \pm 0.03\%$ ,  $0.65 \pm 0.03\%$  and  $0.82 \pm 0.06\%$  of chromium. Within each of these four series the molybdenum content is varied from zero to approximately 0.60%. Complete analyses are given in Table I. The high values of sulphur relative to those of phosphorus arose from the particular type of pig iron used for recarburisation.

### (2) Testing Procedure.

The Jominy test-pieces were in all cases machined from normalised bar samples. The form of test-piece used consisted of a cylinder  $3\frac{7}{8}$  in. long  $\times$  1 in. in dia. with a flange at one end  $1\frac{1}{8}$  in. in dia.  $\times \frac{1}{8}$  in. thick. A hole 1 in. deep by  $\frac{3}{16}$  in. in dia. was drilled from the flanged end down the axis of the test-piece to accommodate the thermocouple used to control the heating before end-quenching.

TABLE I.—Analyses of the Steels Tested.

Steel No.	C. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	Mo. %.	Al. %.
1	0.30	0.63	0.20	0.036	0.020	0.92	Nil	Nil	0.020
2	0.30	0.54	0.22	0.032	0.016	0.86	0.20	Nil	0.013
3	0.31	0.50	0.22	0.033	0.018	0.87	0.20	0.15	0.015
4	0.31	0.53	0.21	0.032	0.018	0.87	0.21	0.25	0.011
5	0.30	0.52	0.22	0.032	0.016	0.88	0.21	0.42	0.022
6	0.30	0.58	0.18	0.036	0.019	0.89	0.41	Nil	0.018
7	0.33	0.62	0.21	0.045	0.021	0.89	0.47	0.13	0.018
8	0.31	0.52	0.19	0.037	0.016	0.91	0.43	0.23	0.020
9	0.31	0.63	0.20	0.040	0.020	0.91	0.41	0.33	0.016
10	0.29	0.58	0.17	0.038	0.019	0.88	0.44	0.58	0.013
11	0.32	0.64	0.18	0.041	0.019	0.89	0.68	Nil	0.013
12	0.32	0.61	0.19	0.041	0.020	0.90	0.64	0.11	0.013
13	0.35	0.57	0.20	0.032	0.021	0.89	0.65	0.22	0.011
14	0.32	0.58	0.19	0.034	0.021	0.90	0.63	0.35	0.013
15	0.33	0.60	0.19	0.038	0.021	0.86	0.62	0.61	0.013
16	0.34	0.58	0.20	0.035	0.020	0.89	0.88	Nil	0.018
17	0.37	0.58	0.25	0.033	0.022	0.88	0.81	0.20	0.011
18	0.35	0.70	0.24	0.033	0.021	0.89	0.87	0.34	0.013
19	0.32	0.64	0.18	0.037	0.024	0.89	0.77	0.57	0.011

During the heating period the specimen was immersed in cast-iron turnings to minimise scaling. The test-piece was heated to the quenching temperature in 30–40 min. and held at temperature for a specified time before transference to the quenching fixture, which was of the standard type recommended by the Society of Automotive Engineers.<sup>(1)</sup>

The water for the quenching jet was supplied from an overhead tank, by which means a constant pressure of water was maintained. The free height of the jet was controlled to  $2\frac{1}{2}$  in. by means of a valve, the setting of which was checked periodically. An additional valve was used to stop and start the jet.

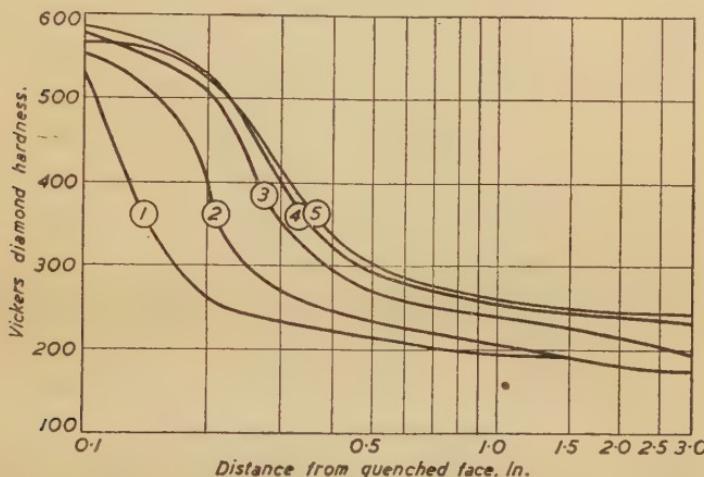


FIG. 1.—Jominy Hardenability Curves for Steels Nos. 1 to 5.

When the test-piece was cold, longitudinal flats were ground on the specimen  $180^\circ$  apart and 0·015 in. deep. This operation was performed, with extreme care to avoid local heating, on a surface grinder supplied with copious water-cooling. The flats were finally polished on grade 0 emery paper before hardness testing. All hardness readings were obtained on the Vickers diamond hardness testing machine, using a 30-kg. load.

### (3) Effect of Quenching Temperature and Soaking Time.

The hardenability curves obtained from specimens soaked for 20 min. at  $880^\circ$  C. are reproduced in Figs. 1 to 4. The distance factor in these curves is plotted on a logarithmic scale and the numbers on the curves correspond to the steel numbers given in Table I.

Curves identical within the experimental error were obtained when the series was repeated with the soaking time increased to

60 min. Specimens of steels 1, 6, 7, 9, 11, 15, 16 and 19 were end-quenched from 850° C. after 20 min. at temperature. The

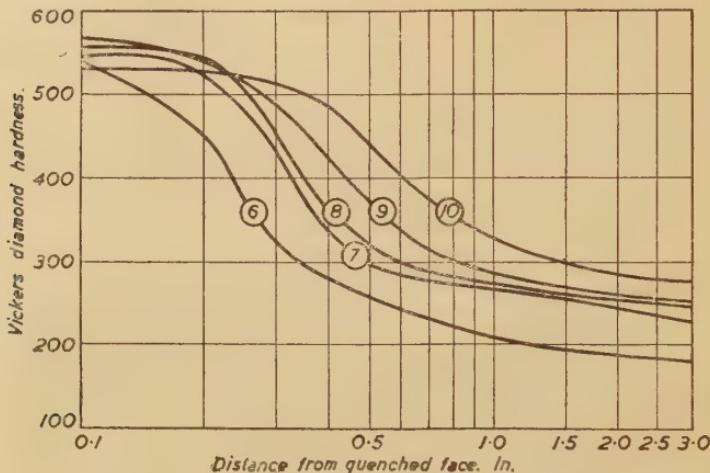


FIG. 2.—Jominy Hardenability Curves for Steels Nos. 6 to 10.

curves obtained were the same as those obtained in the first two series of experiments.

#### (4) Interpretation of Hardenability Curves.

The distance from the quenched face to the point of inflection of the Jominy curve was taken as a measure of the hardenability.

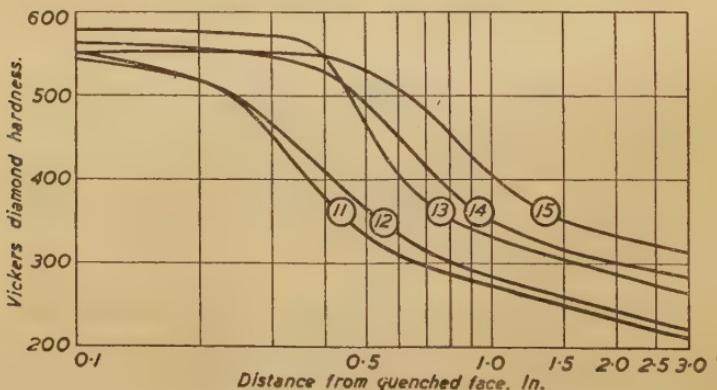


FIG. 3.—Jominy Hardenability Curves for Steels Nos. 11 to 15.

In most cases this could be readily determined visually, but, especially in the case of the deep-hardening steels, it was considered necessary to locate the point of inflection by plotting distance-

gradient graphs. Where the gradient curve indicated that the maximum gradient was maintained over an appreciable distance, the mid-point of this linear part of the curve was taken as the point of assessment. In every case the inflection point occurred at or near the centre of the steep part of the Jominy curve. Data deduced by this method of interpretation will therefore correspond closely to the transition zone as determined by etching and fracture tests.

The curves published by Grossmann<sup>(2)</sup> and by Grossmann, Asimow and Urban<sup>(3)</sup> were used to interpret these distances in terms of equivalent critical diameters for different values of Grossmann's quenching factor  $H$ . The Jominy distance figures and the equivalent ideal critical diameters are given in Table II.

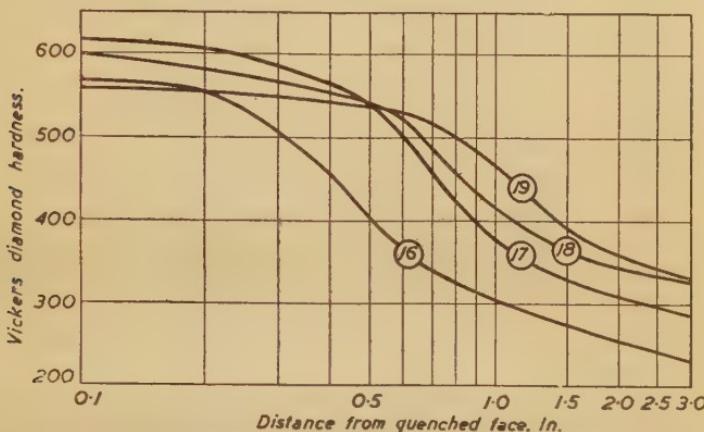


FIG. 4.—Jominy Hardenability Curves for Steels Nos. 16 to 19.

#### (5) Austenitic Grain Size.

In order to test Grossmann's formula<sup>(2)</sup> for calculating the equivalent diameter for an ideal quench ( $D_\infty$ ), the austenitic grain sizes of the steels at the moment of quenching were determined. To do this a micro-surface prepared on the Jominy test-piece itself was etched in 2% nital solution. The austenitic grain size was then measured in the "transition zone" where the original austenitic grains were clearly outlined by troostite. The figures obtained are given in Table III. For the sake of comparison, figures obtained by the standard McQuaid-Ehn method on small normalised sections are also included in this Table.

#### (6) Grossmann's Hardenability Formula.

The equivalent diameter for an ideal quench was calculated for each of the steels on the basis of Grossmann's formula<sup>(2)</sup> connecting the chemical composition and grain size with the hardenability.

TABLE II.—*Jominy Distance Figures and Equivalent Ideal Critical Diameters.*

Steel No.	Vickers Diamond Hardness at Point of Inflection.	Distance to Inflection Point. In.			Equivalent Ideal Critical Diameter. In.			
		20 min. at 880° C.	60 min. at 880° C.	20 min. at 850° C.	20 min. at 880° C.	60 min. at 880° C.	20 min. at 850° C.	Average.
1	350	0.150	0.140	0.145	1.38	1.34	1.36	1.36
2	365	0.225	0.210	...	1.72	1.66	...	1.69
3	380	0.275	0.270	...	1.94	1.92	...	1.93
4	400	0.295	0.300	...	2.03	2.05	...	2.04
5	405	0.305	0.307	...	2.07	2.05	...	2.06
6	350	0.265	0.275	0.265	1.90	1.94	1.90	1.91
7	390	0.335	0.330	0.350	2.20	2.17	2.25	2.21
8	390	0.360	0.360	...	2.30	2.30	...	2.30
9	400	0.450	0.420	0.450	2.67	2.55	2.67	2.63
10	400	0.580	0.530	...	3.15	2.98	...	3.06
11	390	0.390	0.395	0.390	2.42	2.45	2.42	2.43
12	400	0.410	0.440	...	2.50	2.63	...	2.56
13	415	0.590	0.540	...	3.20	3.00	...	3.10
14	425	0.670	0.640	...	3.50	3.38	...	3.44
15	425	0.880	0.880	1.00	4.18	4.18	4.50	4.29
16	410	0.480	0.470	0.510	2.79	2.74	2.90	2.81
17	445	0.750	0.660	...	3.77	3.45	...	3.61
18	455	0.810	0.850	...	3.97	4.10	...	4.03
19	450	1.100	0.900	1.15	4.75	4.25	4.87	4.62

The values obtained are compared in Table IV. with those obtained experimentally.

Grossmann indicates that the multiplying factor for chromium varies linearly with the chromium content up to 0.30% of chromium, and beyond that it depends upon the degree of solution of the carbides. Consequently, in the three series of steels of high chromium

TABLE III.—*Austenitic Grain Sizes of the Steels.*

Steel No.	A.S.T.M. Grain Size.		Steel No.	A.S.T.M. Grain Size.	
	McQuaid-Ehn.	From Test Specimen.		McQuaid-Ehn.	From Test Specimen.
1	6-7	8	11	6-4	6
2	5-6	6½	12	4-3	5½
3	6	6½	13	5	6
4	6	6½	14	4-3	6½
5	6	6½	15	5-4	6
6	6	7½	16	4	5½
7	6-5	6½	17	5-4	5½
8	5-4	6	18	6-5	6
9	6-5	6	19	4	6
10	5-4	6			

content the hardenability is indicated as a range. The upper limit of this range was calculated by using the chromium factor obtained by linear extrapolation of the lower part of Grossmann's curve.

TABLE IV.—*Equivalent Ideal Critical Diameters of Steels, Calculated and Determined.*

Steel No.	Equivalent Ideal Critical Diameter. In.		
	As calculated by Grossmann's Formula.	As calculated by the Grossmann-Crafts Formula.	Average Experimental Value.
1	0·90-0·90	1·00-1·00	1·36
2	1·30-1·30	1·40-1·40	1·69
3	1·85-1·85	2·00-2·00	1·93
4	2·40-2·40	2·60-2·60	2·04
5	3·00-3·00 *	3·25-3·25*	2·06
6	1·50-1·65	1·65-1·80	1·91
7	2·70-3·05	2·95-3·30	2·21
8	2·80-3·10	3·05-3·35	2·30
9	3·80-4·10 *	4·20-4·50*	2·63
10	4·70-5·15 *	5·20-5·70*	3·06
11	2·10-2·65	2·35-2·95	2·43
12	2·85-3·55	3·15-3·90	2·56
13	3·50-4·35	3·90-4·80	3·10
14	4·00-4·90 *	4·40-5·40*	3·44
15	5·90-7·15 *	6·50-7·85*	4·29
16	2·40-3·20	2·60-3·55	2·81
17	4·10-5·40	4·50-5·95	3·61
18	5·60-7·60 *	6·20-8·40*	4·03
19	6·20-8·15 *	6·85-9·00*	4·62

\* Molybdenum factor obtained by linear extrapolation of Grossmann's curve.

The lower limit was calculated by using the lowest chromium factor indicated by Grossmann for each particular chromium content.

The molybdenum multiplying factor for twelve of the steels was obtained from Grossmann's curve, but for the remaining steels containing more than 0·25% of molybdenum it was necessary to extrapolate this curve linearly. The equivalent ideal critical temperatures calculated by using these extrapolated factors, which are included in Table IV. for the sake of completeness, are indicated by an asterisk and should not be taken into account when assessing the accuracy of Grossmann's formula.

It will be noted that the calculated values are low in the shallow-hardenning and high in the deeper-hardenning steels. Table IV. also includes ideal critical diameters as calculated from Grossmann's formula as modified by Crafts.<sup>(4)</sup> On the average these figures show a wider discrepancy than those obtained from Grossmann's original formula.

(7) *Iso-Hardenability Curves.*

In order to obtain a broad view of the effect of chromium (Cr, weight-%) and molybdenum (Mo, weight-%) on the hardenability of the type of steel investigated, the following equation was fitted to the ideal critical diameter values ( $D_{\infty}$  inch) given in Table II., and shown in graphical form in Figs. 5 and 6 :

$$D_{\infty} = 2.36 \text{ Cr}^2 \text{Mo} + 2.00 \text{ CrMo} + 0.60 \text{ Mo} + 1.70 \text{ Cr} + 1.31.$$

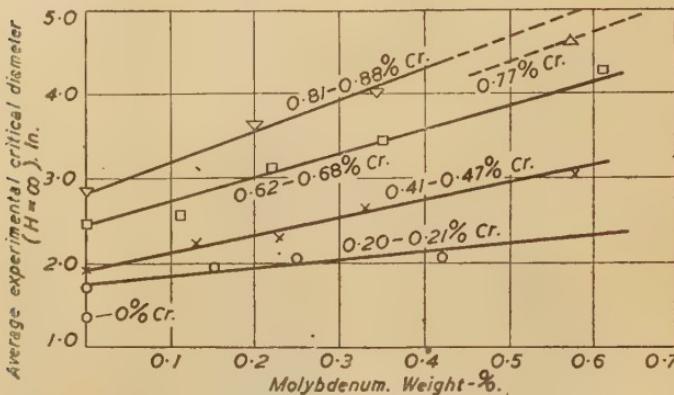


FIG. 5.—Effect of Molybdenum on the Ideal Critical Diameter of Steels containing  $0.20 \pm 0.01\%$ ,  $0.44 \pm 0.03\%$ ,  $0.65 \pm 0.03\%$  and  $0.85 \pm 0.04\%$  of Chromium.

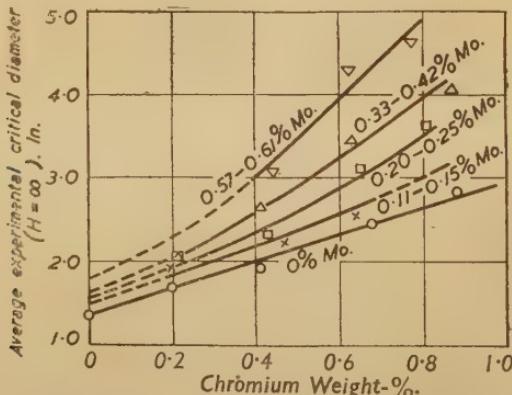


FIG. 6.—Effect of Chromium on the Ideal Critical Diameter of Steels containing no Molybdenum,  $0.13 \pm 0.02\%$ ,  $0.23 \pm 0.03\%$ ,  $0.37 \pm 0.05\%$  and  $0.59 \pm 0.02\%$  of Molybdenum.

It must be fully realised that the application of this equation is limited to steels of a foundation analysis similar to those tested, i.e. :

Carbon.	Manganese.	Silicon.	Nickel.
0.33%	0.60%	0.20%	0.90%

containing between 0·2% and 0·9% of chromium and between zero and 0·6% of molybdenum. The agreement between the experimental figures and the values calculated from the formula is illustrated in Table V.

Using this equation, it is possible to calculate the  $D_{\infty}$  value of any steel within the specified range of analysis, or, conversely, the percentages of chromium and molybdenum required to produce a steel possessing a given ideal critical diameter ( $D_{\infty}$ ). Data of this

TABLE V.—*Comparison of Experimental and Calculated Values for the Ideal Critical Diameter.*

Steel No.	Ideal Critical Diameter. In.		
	Experimental Value.	Calculated Value.*	Difference between Calculated and Average Experimental Value.
1	1·34-1·38	1·31	-0·05
2	1·66-1·72	1·65	-0·04
3	1·92-1·94	1·81	-0·12
4	2·03-2·05	1·95	-0·09
5	2·05-2·07	2·14	+0·08
6	1·90-1·94	2·01	+0·10
7	2·17-2·25	2·38	+0·17
8	2·30-2·30	2·48	+0·18
9	2·55-2·67	2·61	-0·02
10	2·98-3·15	3·18	+0·12
11	2·42-2·45	2·46	+0·03
12	2·50-2·63	2·71	+0·15
13	3·00-3·20	3·05	-0·05
14	3·38-3·50	3·36	-0·08
15	4·18-4·50	4·04	-0·25
16	2·74-2·90	2·81	0·00
17	3·45-3·77	3·44	-0·17
18	3·97-4·10	4·19	+0·16
19	4·26-4·87	4·63	+0·01

\* Using the formula :  $D_{\infty} = 2·36 \text{ Cr}^2\text{Mo} + 2·00 \text{ CrMo} + 0·60 \text{ Mo} + 1·70 \text{ Cr} + 1·31$ .

nature are given in Table VI. As an example of the use of this Table it is noted that a steel containing :

Carbon. 0·33%	Manganese. 0·60%	Silicon. 0·20%	Nickel. 0·90%
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requires 0·70% of chromium, or 0·60% of chromium + 0·06% of molybdenum, or 0·50% of chromium + 0·16 of molybdenum, &c., to give a hardenability equivalent to an ideal critical diameter of 2·5 in. The Table can also be used to obtain the ideal critical diameter of a steel of known analysis.

Probably a more convenient method of representing these data is that shown in Fig. 7, where iso-hardenability lines are plotted

against the chromium and molybdenum contents. This diagram may be used to obtain the same information as that given in Table VI.

TABLE VI.—*Molybdenum and Chromium Contents required to Produce Desired Hardenability.*

Ideal Critical Diameter. In.	Molybdenum, %, required together with—							
	0·2% Cr.	0·3% Cr.	0·4% Cr.	0·5% Cr.	0·6% Cr.	0·7% Cr.	0·8% Cr.	0·9% Cr.
2·0	0·31	0·13	0·02	...	...	...	...	...
2·5	...	0·48	0·30	0·16	0·06	0·00	...	...
3·0	...	...	0·58	0·38	0·26	0·16	0·09	0·04
3·5	...	...	...	0·61	0·44	0·32	0·23	0·15
4·0	...	...	...	...	0·63	0·48	0·36	0·27
4·5	...	...	...	...	...	0·64	0·50	0·38
5·0	...	...	...	...	...	...	0·63	0·50

All the above data can be reduced to critical diameters corresponding to any given rate of quenching, provided that the value

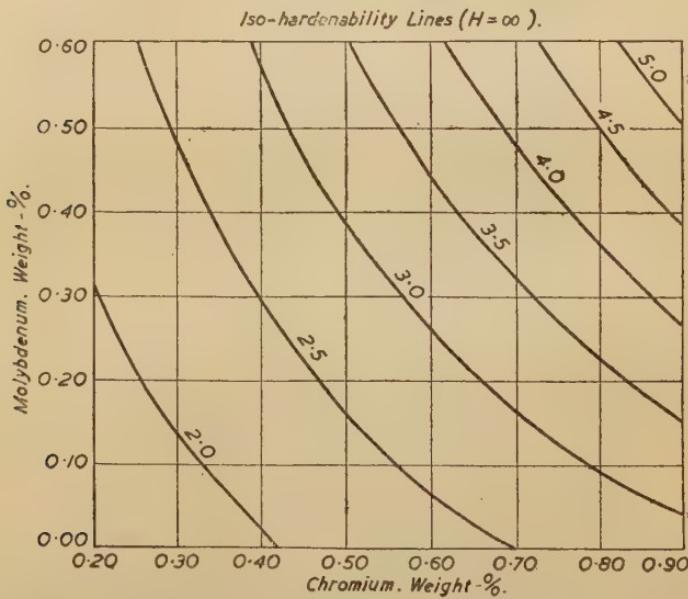


FIG. 7.—Effect of Additions of Chromium and Molybdenum on the Ideal Critical Diameter of Steel No. 1 ( $H = \infty$ ).

of  $H$  has been ascertained, by means of the curves published by Grossmann, Asimow and Urban.<sup>(3)</sup> As an example, in Fig. 8 iso-hardenability curves are drawn corresponding to a quenching factor

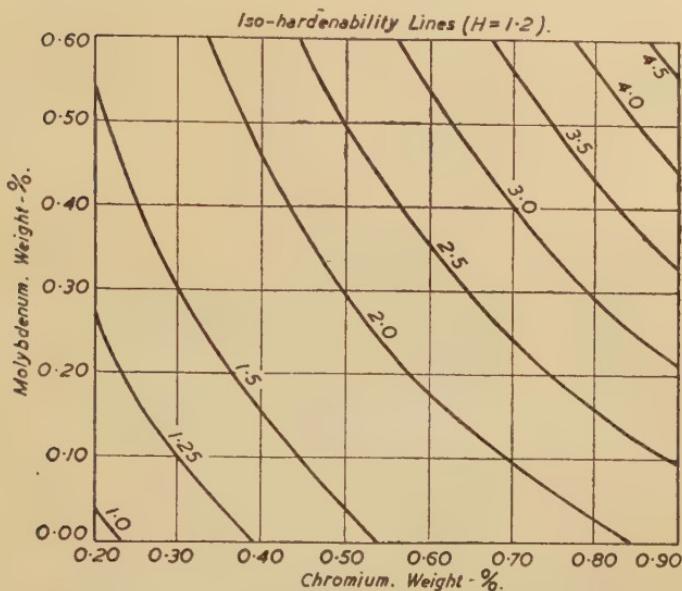


FIG. 8.—Effect of Chromium and Molybdenum Additions on the Critical Diameter of Steel No. 1 quenched in water ( $H = 1\cdot2$ ).

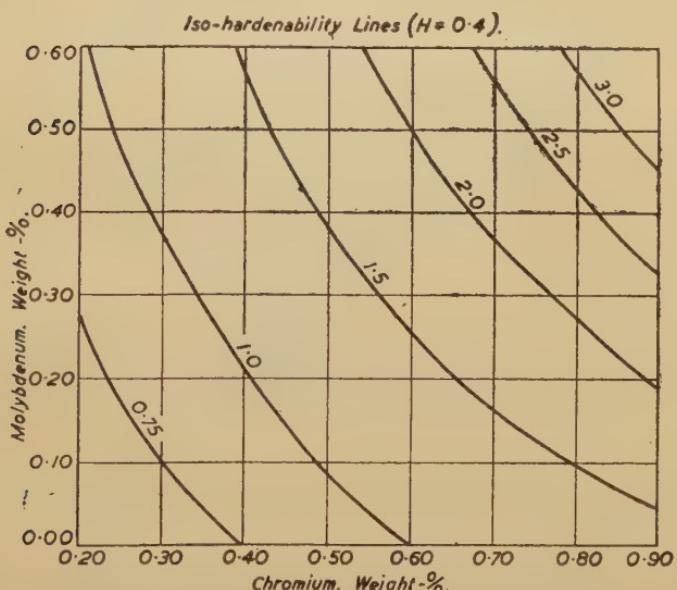


FIG. 9.—Effect of Chromium and Molybdenum Additions on the Critical Diameter of Steel No. 1 quenched in oil ( $H = 0\cdot4$ ).

of  $H = 1.2$ . From this figure it is possible, therefore, to obtain directly the critical diameter of a steel in this series when quenched in slightly agitated water. In a similar manner the iso-hardenability diagram corresponding to a quench in moderately agitated oil was drawn by taking  $H = 0.4$  (Fig. 9).

### (8) Conclusions.

The effect on the hardenability of simultaneous additions of chromium and molybdenum to a grain-size-controlled steel (A.S.T.M. grain size  $6\frac{1}{2} \pm 1$ ) conforming to the following specification has been investigated by the Jominy end-quench method :

Carbon.	Manganese.	Silicon.	Sulphur.	Phosphorus.	Nickel.
$0.33 \pm 0.04\%$	$0.60 \pm 0.10\%$	$0.21 \pm 0.04\%$	$0.039 \pm 0.007\%$	$0.020 \pm 0.004\%$	$0.89 \pm 0.03\%$

by weight.

The investigation covered the range zero to  $0.61\%$  of molybdenum and  $0.20$ – $0.88\%$  of chromium.

The experimental results appear to warrant the following conclusions :

(1) The hardenability of these steels does not alter as the quenching temperature is raised from  $850^\circ$  C. to  $880^\circ$  C. or as the soaking time before quenching is increased from 20 min. to 60 min.

(2) The equivalent ideal critical diameters for these steels do not conform closely to the equation formulated by Grossmann relating them with the chemical composition and austenitic grain size.

(3) Grossmann's hardenability equation as modified by Crafts agrees with the author's experimental results to a less extent than does Grossmann's original formula.

(4) The equivalent ideal critical diameters ( $D_\infty$  inch) for these steels conform within the experimental error to the following equation, when the chromium and molybdenum contents are expressed as weight percentages :

$$D_\infty = 2.36 \text{ Cr}^2\text{Mo} + 2.00 \text{ CrMo} + 0.60 \text{ Mo} + 1.70 \text{ Cr} + 1.31.$$

(5) By means of the above equation it was possible to tabulate the chemical compositions required to produce a steel possessing a given ideal critical diameter, and to draw an iso-hardenability curve showing the variation of hardenability as the chromium and molybdenum contents varied.

(6) By means of curves published by Grossmann, Asimow and Urban the above-mentioned iso-hardenability diagram was redrawn so as to indicate directly the critical diameter of a steel quenched in slightly agitated water ( $H = 1.2$ ).

(7) A third iso-hardenability diagram was drawn to indicate the critical diameter of these steels when quenched in moderately agitated oil ( $H = 0.4$ ).

*Acknowledgment.*

This research was instigated by and carried out under the direction of Mr. D. A. Oliver, M.Sc., F.Inst.P., Director of Research, Messrs. William Jessop & Sons, Ltd., Sheffield. It is a pleasure to acknowledge his valuable advice and encouragement.

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  - (3) M. A. GROSSMANN, M. ASIMOW and S. F. URBAN : American Society for Metals, Symposium on Hardenability of Alloy Steels, 1939, p. 124.
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## CORRESPONDENCE.

Mr. WALTER CRAFTS (Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N.Y., U.S.A.) wrote : Dr. Steven has made a practical correlation of the hardenability attainable and the alloy content in the nickel-chromium-molybdenum steel investigated. Although somewhat greater deviations might be expected to result from less accurate control of the composition and grain size in commercial production, it would appear to be feasible to maintain the hardenability of this steel within a relatively narrow range.

The manner of expressing the effects of chromium and molybdenum on hardenability, as shown in Fig. 7 and the corresponding equation, is very informative in that the effect of the alloy is readily visualised in terms of the ideal critical diameter of the steel. It cannot be emphasised too strongly that the relation is significant only for the composition on which it was determined and, even with appropriate modifications, does not appear to be adaptable to general application. Although it has been found that microscopic determination is necessary to establish Grossmann multiplying factors,<sup>1</sup> Dr. Steven has demonstrated that estimates based on the Jominy hardness curve can be used effectively within a limited range.

The divergence from the hardenability calculated according to Grossmann's principle has been noted in several types of low-carbon steels. The subject has not been studied sufficiently to define the degree to which different steels are affected. However,

<sup>1</sup> W. Crafts and J. L. Lamont, *American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1657: Metals Technology*, 1944, vol. 11, Jan., No. 1.

it has appeared that the tendency towards the rejection of ferrite during quenching has a major influence. For this reason the estimation of martensite by the inflection of the Jominy hardness curve is subject to some error, as the hardness of the non-martensitic constituents is relatively low when ferrite is one of the components. The more or less intangible quality factors, such as the degree of microsegregation, also appear to affect the hardenability strongly in the low-carbon steels.

It would appear that some modification of the Grossmann factors is desirable in the low-carbon range, but, in spite of minor divergences, the Grossmann principle for calculating hardenability is extremely useful. The advantages of a more extensive study of a specific composition range are also illustrated by the precise and practical investigation of Dr. Steven. He is to be congratulated on having established a very useful relation that should facilitate greater utilisation of nickel-chromium-molybdenum steel in which the alloying elements are derived mainly from scrap.

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#### AUTHOR'S REPLY.

Dr. STEVEN wrote in reply : In view of Mr. Crafts' well-known contributions on hardenability to the American literature his comments were received with great pleasure. It is of particular interest to note that he also holds the opinion that Grossmann's approach must be modified for certain classes of steel.

Mr. Crafts' major criticism appears to be directed against the choice of the inflection point as a method of assessing hardenability from Jominy hardenability curves. This point was selected because it was considered to be the only unequivocal point on the curves suitable for a correlation of the kind attempted. Other methods of interpretation involved additional assumptions and were finally rejected in favour of the inflection point. Experimental work carried out in our Research Laboratory since the publication of the paper appears to endorse fully this particular choice.

The effects of grain size and of elements other than chromium and molybdenum were not determined, and therefore it is agreed that the proposed relationship cannot be used for steels outside the range of those examined. It is believed, however, that the method outlined in this paper is a particularly convenient one for exploring the variation of hardenability within a given group of steels.

# THE SCALING PROPERTIES OF STEELS IN FURNACE ATMOSPHERES AT 1150° C.\*

BY A. PREECE, M.Sc., AND R. V. RILEY, PH.D. (THE UNIVERSITY,  
LEEDS).

(Figs. 13 to 28 = Plates X. to XIII.)

*Paper No. 14/1943 of the Alloy Steels Research Committee.*

## SUMMARY.

The rate of oxidation and the character of the oxide formed in furnace atmospheres at 1150° C. were examined for a selection of carbon and alloy steels. An account is given of the important influence of sulphur dioxide and free oxygen in the furnace atmosphere in governing the process of oxidation. It was found that each of the alloy steels behaved in a characteristic manner, and generalisations are difficult. The formation of sulphide complexes at the scale-metal interface observed in earlier experiments at 1000° C. also occurred at 1150° C., and they behaved in a similar manner by inducing intercrystalline penetration of scale into the metal in all the steels except those containing appreciable quantities of silicon, chromium and aluminium. With these three latter types of steels preferential oxidation of the alloying element produced a protective oxide film, and continued oxidation was possible only under conditions of temperature and furnace atmosphere where the film became unstable. Factors which influence the instability of these films are discussed.

THE present paper describes results obtained in a survey of the scaling characteristics of a selection of steels in furnace atmospheres at 1150° C. It forms part of a more comprehensive study which covers the whole range of heat-treatment, forging and soaking-pit temperatures found in practice. Results obtained in a similar investigation at 1000° C. have already been published,<sup>(1)</sup> and a survey at temperatures above 1150° C. is at present in progress at Leeds University.

A review of published work on the oxidation of steel was given in an earlier report,<sup>(1)</sup> and attention is also drawn to the extensive review<sup>(2)</sup> published by the late Dr. Hatfield.

## EXPERIMENTAL PROCEDURE.

Weighed specimens of steel were heated to 1150° C. in pure nitrogen, then exposed to the furnace atmosphere for 1½ hr., after which they were cooled to room temperature in nitrogen and again weighed.

A description of the apparatus and experimental procedure was

\* Received November 16, 1943. This paper is published by authority of the Alloy Steels Research Committee. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

given in an earlier publication.<sup>(3)</sup> The only modification made in the apparatus for the present survey was the substitution of a gas-heated furnace in place of an electrically heated one. With this gas-heated furnace, a constant-temperature zone of 4 in. was obtained at 1150° C., and with reasonable attention the temperature could be maintained to within  $\pm 5^\circ$  C.

A mixture of gases consisting of 80% nitrogen, 10% water vapour and 10% carbon dioxide was adopted as a basic furnace atmosphere for this work. It represents roughly the products of complete combustion of producer gas and fuel oil. With suitable additions of carbon monoxide an atmosphere resembling that obtained by incomplete combustion of the fuel was produced. Additions of

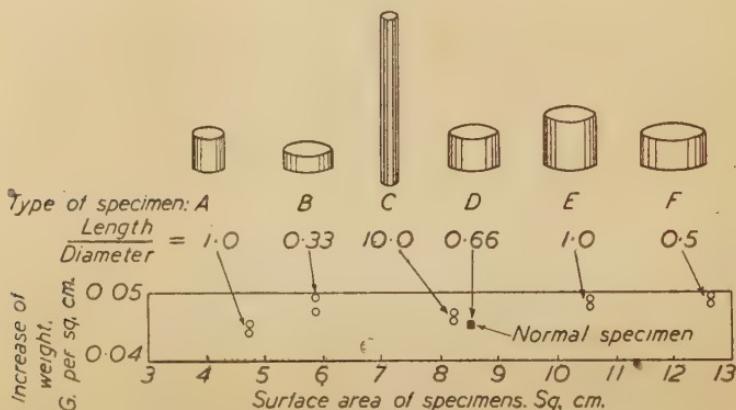


FIG. 1.—Effect of Size and Shape of Specimen on Rate of Scale Formation.

oxygen, on the other hand, gave an atmosphere such as would result from the use of excess air in burning the fuel.

In fuel technology, furnace atmospheres are described as neutral, reducing or oxidising according to whether they are free from or contain either carbon monoxide or free oxygen, respectively. It will be understood that such terms refer only to the composition of the atmosphere and are in no way concerned with its effect on steels exposed to it. In the following text the basic atmosphere described above is referred to as the neutral atmosphere.

As in the earlier investigations,<sup>(1, 3)</sup> the figure for the increase in weight per unit area was taken as a measure of the oxidation of the steel. It was found experimentally that the size and shape of the specimen do not appreciably affect this figure. This is demonstrated in Fig. 1, where the results are plotted for specimens which differ widely in both size and shape.

During preliminary experiments it became evident that slight errors in temperature measurement could arise, owing to loss of

heat by radiation from the tip of the thermocouple sheath to the cool end of the furnace. The thermocouple sheath extended to the centre of the constant-temperature zone, and it was observed that when the thermocouple was not quite in contact with the end of the sheath, *i.e.*, position 1 in Fig. 2, the temperature recorded was slightly higher than when the couple made contact with the end of the sheath, *i.e.*, position 2. This difference in temperature was negligible at 700° C., but increased to 4.5° at 1200° C., as shown by the curve in Fig. 2.

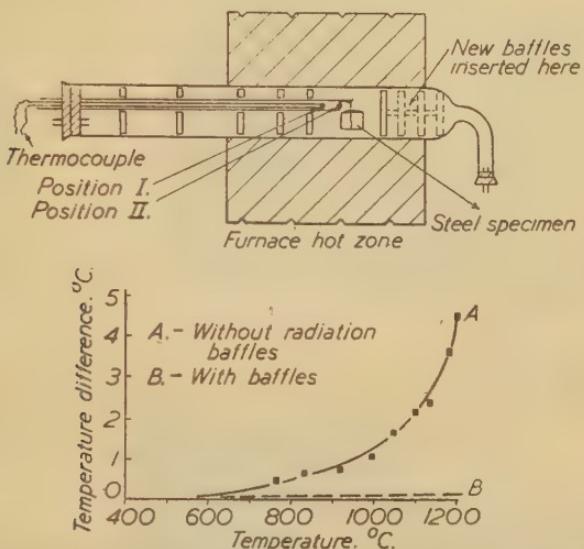


FIG. 2.—Error in Temperature Measurement due to Radiation to Cold End of Furnace Tube.

This temperature difference remained the same whether the furnace tube contained a stationary atmosphere or had gas flowing through it. The chilling of the end of the thermocouple sheath was not due to the gas flowing over it and therefore could only be accounted for by heat lost by radiation to the cool end of the furnace tube. By inserting refractory discs in the leading end of the tube, as shown in Fig. 2, black-body conditions were obtained and the thermocouple showed no difference in temperature when transferred from position 1 to position 2.

It has been amply demonstrated in other publications that when metal specimens are exposed to a stream of oxidising gas the rate of oxidation increases with the rate of gas flow over the surface of the specimen, until a critical velocity is reached, above which the rate of oxidation remains constant and is independent of the rate of gas flow. This critical velocity depends on a number of factors, such as the size of specimen, composition of the atmosphere,

temperature, &c., and must be determined for each set of conditions. Fig. 3 shows curves obtained for two typical furnace atmospheres. The critical velocity for the most active of the furnace atmospheres used was found to be 30 ft. per min. and the standard figure of 60 ft. per min. adopted in the present investigation was well above this critical velocity.

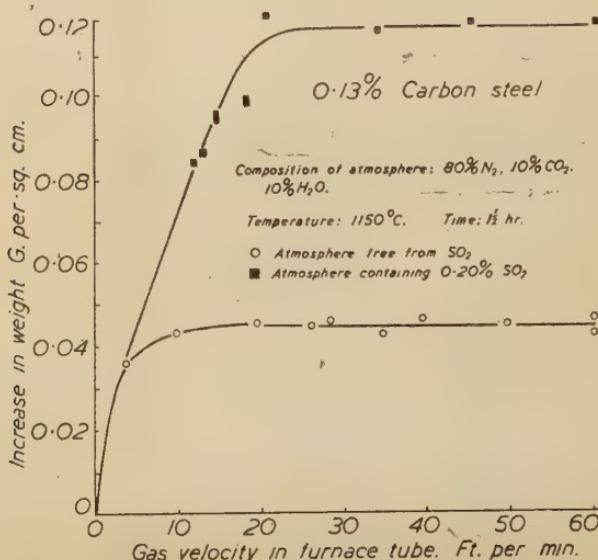


FIG. 3.—Relationship between Velocity of Furnace Atmosphere over Surface of Specimen and Rate of Scale Formation.

#### SCALING PROPERTIES OF STEELS AT 1150° C.

The compositions of the steels used in the present investigation are recorded in Table I. All the steels were supplied as forged or rolled bars. The bars were machined to 0.60 in. in dia.; specimens 0.4 in. long were then sawn from the machined bar and polished to 00 emery paper.

#### Plain Carbon Steels.

The scaling properties of the 0.13% and the 1.3% carbon steels were very similar in all respects. The type of scale produced and the character of the scale-metal interface were identical in all the atmospheres used in the present investigation; there was, however, a lower rate of scale formation with the high-carbon steel in the neutral atmosphere. The lower rate of scaling of the 1.3% carbon steel was not maintained when SO<sub>2</sub> or oxygen was added to the

## PLATE X.



Fig. 13.—Crystalline Surface of Scale produced on 0.13% Carbon Steel in Neutral Furnace Atmosphere in  $1\frac{1}{2}$  hr. at  $1150^{\circ}\text{C}$ .  $\times 12.5$ .



Fig. 14.—Massive FeO and FeO-FeS Eutectic in Section of Scale formed on Carbon Steel in Neutral Furnace Atmosphere containing 0.2% of  $\text{SO}_2$ .  $\times 300$ .



Fig. 15.—0.13% Carbon Steel.  
Figs. 15 and 16.—Decarburisation during Exposure to Neutral Furnace Atmosphere for  $1\frac{1}{2}$  hr. at  $1150^{\circ}\text{C}$ .  $\times 12.5$ .



Fig. 16.—1.3% Carbon Steel.

(Illustrations reduced to nine-tenths linear in reproduction.)

*[Preece and Riley,  
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FIG. 18.—Intercrystalline Penetration of Scale into 5% Nickel Steel after 1½ hr. Exposure to Neutral Atmosphere containing 0.2% of  $\text{SO}_2$  at 1150° C.  $\times 600$ .



FIG. 17.—Effect of Oxygen Additions to Neutral Furnace Atmosphere, containing 0.2% of  $\text{SO}_2$  on Scale formed on 13% Manganese Steel, (a) 0.5%, (b) 1%, (c) 3% of oxygen added.  $\times 1$ .

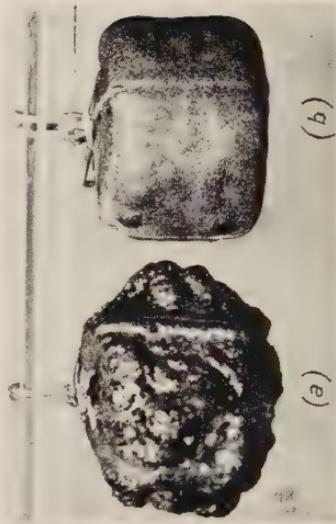


FIG. 20.—Effect of Oxygen Addition to Sulphurous Furnace Atmosphere on Scale formed on 4% Silicon Steel exposed for 1½ hr. at 1150° C. (a) 80% N, 10%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O} + 0.2\% \text{SO}_2$ , (b) 75% N, 10%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O} + 0.2\% \text{SO}_2 + 5\% \text{O}_2$ .  $\times 1$ .



FIG. 19.—Decarburisation and Crystal Growth in Surface Layers of 4% Silicon Steel after 1½ hr. in Neutral Oxidising Furnace Atmosphere containing 5% of Oxygen at 1150° C.  $\times 300$ .

(Illustrations reduced to nine-tenths linear in reproduction.)

[Preece and Riley.]

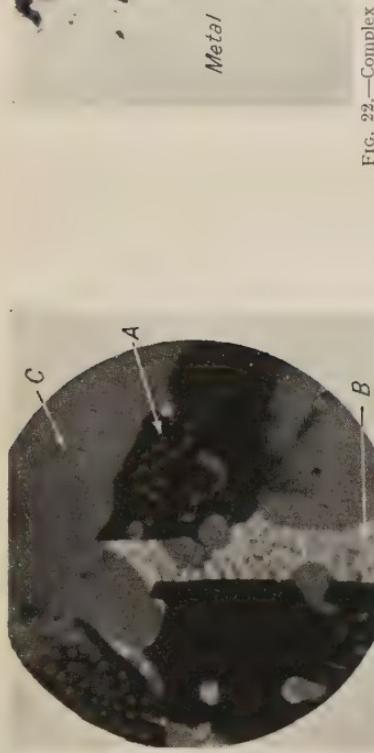


FIG. 21.—Scale formed on 4% Silicon Steel at 1150° C. in Neutral Furnace Atmosphere containing  $0.2\%$  of  $\text{SO}_2$ . (a) Fayalite-FeO eutectic. (b) FeO-FeS eutectic. (c) Massive FeO.  $\times 10(10)$ .

FIG. 22.—Complex Inner Layer of Scale formed on 12% Chromium Steel in Neutral Furnace Atmosphere containing  $0.2\%$  of  $\text{SO}_2$  exposed for  $1\frac{1}{2}$  hr. at 1150° C.  $\times 200$ .



FIG. 23.—Breakdown of Protective Film on 18% Chromium, 21% Nickel Steel at 1150° C. in Neutral Furnace Atmosphere +  $0.2\%$  of  $\text{SO}_2$ .  $\times 1$ .



FIG. 24.—Breakdown of Alumina-Rich Protective Film on 8% Aluminium Steel in Neutral Furnace Atmosphere at 1150° C. Black crystals of oxide breaking through.  $\times 12.5$ .

(Illustrations reduced to nine-tenths linear in reproduction.)

[Preece and Riley.]

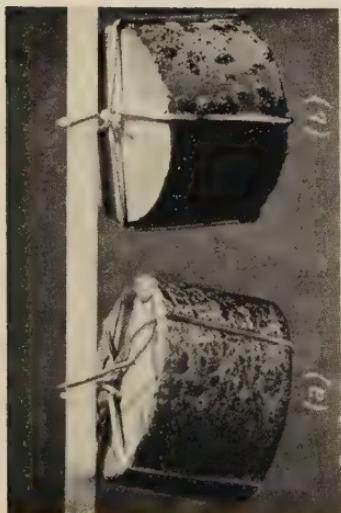


FIG. 25.—Influence of Oxygen in Furnace Atmosphere in Promoting Film Breakdown on 8% Aluminium Steel at 1150° C. Furnace atmosphere containing (a) 2%, (b) no free oxygen.  $\times 1$ .



FIG. 26.—Complex Inner Layer of Scale formed on 8% Aluminium Steel at 1150° C. in Neutral Furnace Atmosphere containing  $\text{SO}_2$ .  $\times 1000$ .



FIG. 27.—Surface of 8% Aluminium Steel immediately below Scale formed at 1150° C. in Furnace Atmosphere containing Sulphur. (a) Penetration of scale into metal. (b) Dark band of sulphide.  $\times 90$ .

(Illustrations reduced to nine-tenths linear in reproduction.)

[Preece and Riley.  
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FIG. 28.—Modified Surface Layer of Metal shown in Fig. 27 at Higher Magnification.  $\times 1000$ .

atmosphere, and with 0·2% of SO<sub>2</sub> or 4% of oxygen in the atmosphere both steels gave very similar results (Fig. 4).

TABLE I.—*Compositions of Steels used in the Present Investigation.*

The principal elements in the steels are set in heavy type.

Steel.	Composition.									
	O. %.	Mn. %.	Si. %.	S. %.	P. %.	Ni. %.	Cr. %.	W. %.	Al. %.	
0·13% carbon . . . .	<b>0·13</b>	0·50	0·10	0·029	0·030	...	...	...	...	
1·30% carbon . . . .	<b>1·30</b>	0·36	0·19	0·014	0·019	...	...	...	...	
5·0% nickel . . . .	0·14	0·35	0·22	0·031	0·038	<b>5·12</b>	...	...	...	
1½% chromium, 3½% nickel . . . .	0·36	0·63	0·14	0·012	0·022	<b>3·59</b>	<b>0·78</b>	...	...	
4% silicon . . . .	0·12	0·14	<b>3·84</b>	0·030	0·042	...	...	...	...	
18% chromium, 8% nickel . . . .	0·11	0·27	0·19	Low	Low	<b>8·50</b>	<b>17·50</b>	...	...	
18% chromium, 2½ nickel . . . .	0·16	0·30	0·45	0·026	0·032	<b>2·50</b>	<b>17·20</b>	...	...	
12% chromium . . . .	0·12	0·25	0·54	0·021	0·026	...	<b>12·60</b>	...	...	
3% silicon, 9% chromium . . . .	0·39	0·88	<b>2·80</b>	0·010	0·020	...	<b>9·00</b>	...	...	
8% aluminium . . . .	0·12	...	...	Low	Low	...	...	...	8·22	
13% manganese . . . .	1·20	<b>13·05</b>	0·49	0·035	0·031	...	...	...	...	
20% chromium, 7% nickel, 4% tungsten . . . .	0·35	0·50	0·50	0·038	0·025	<b>7·00</b>	<b>20·00</b>	<b>4·0</b>	...	
25% chromium, 17% nickel . . . .	0·15	0·55	1·54	0·036	0·028	<b>17·50</b>	<b>24·80</b>	...	...	
30% chromium . . . .	0·37	0·31	0·37	0·020	0·04	...	<b>29·60</b>	...	...	

In the sulphur-free atmosphere, the scale on both steels was similar and consisted of two layers. The outer layer was highly crystalline, as shown in Fig. 13, and was very easily detached,

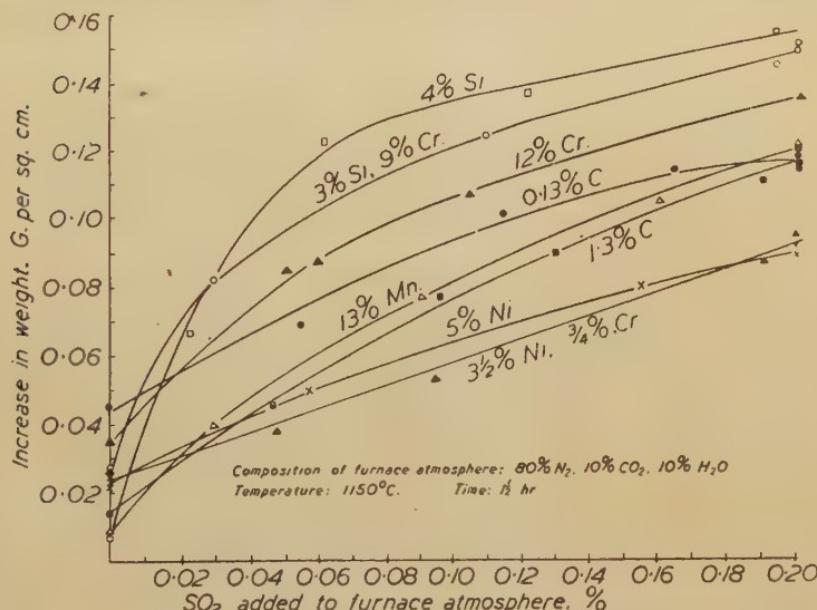


FIG. 4.—Effect of Addition of SO<sub>2</sub> to Neutral Furnace Atmosphere on Rate of Scale Formation.

revealing a finer crystalline inner layer, which could also be removed, though less readily, from the metal surface. With additions of  $\text{SO}_2$  to the atmosphere the scale surface changed gradually from a highly crystalline to a smooth type, until with an atmosphere containing 0.05% of  $\text{SO}_2$  the specimen possessed a flat crazed appearance. With higher concentrations of  $\text{SO}_2$  the surface showed signs of having been semi-molten, and with 0.20% of  $\text{SO}_2$  a very rough disrupted scale was formed in which the macrocrystalline character of the surface was completely obliterated. The scale under these conditions was still made up of two layers, but these were thicker and proved more difficult to remove completely from the specimen.

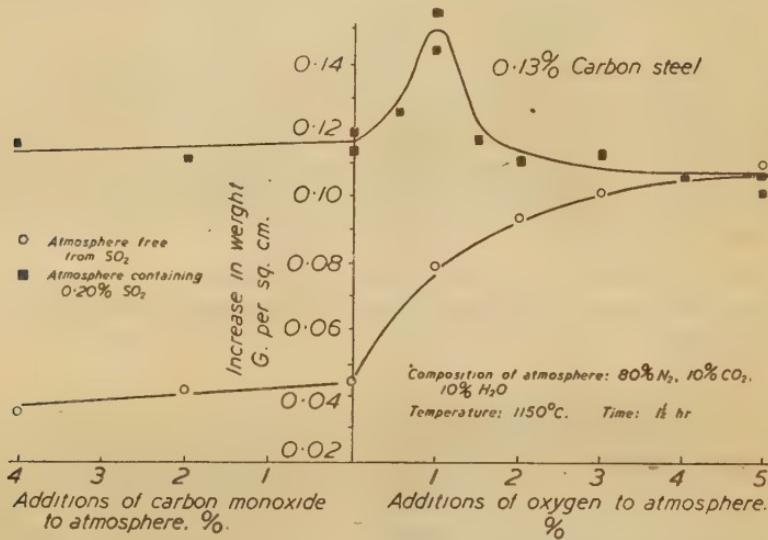


FIG. 5.—Rate of Scale Formation at  $1150^{\circ}\text{C}$ . of 0.13% Carbon Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

The scales formed on the plain carbon steels in the neutral atmosphere containing appreciable quantities of  $\text{SO}_2$  consisted of a layer of iron oxide separated from the steel by an iron-oxide/iron-sulphide eutectic; an example of the eutectic is shown in Fig. 14. The mechanism of scale formation under these conditions proceeds by the solution of iron in the molten sulphide phase at the metal interface and the formation of iron oxide where the molten phase meets the outer iron-oxide layer. A molten phase in contact with the steel at the scaling temperature would thus account for the increased attack. The presence of this oxide-sulphide eutectic was always associated with intercrystalline penetration of the scale into the steel.

In the neutral atmosphere the metal below the scale was decarburised to a depth of approximately 0.04 in. Figs. 15 and 16 were

taken at the same magnification and show respectively the decarburisation of the 0·13% and 1·30% carbon steels after heating for 1½ hr. in the neutral furnace atmosphere. With increasing percentages of  $\text{SO}_2$  in the atmosphere the decarburised band became narrower, until with 0·20% of  $\text{SO}_2$  it disappeared completely. It must be explained that the disappearance of the decarburised band was due simply to the fact that the removal of metal by oxidation became greater than the rate at which carbon diffused through it. It will be evident, therefore, that any change in the composition of the furnace atmosphere which resulted in a greater rate of oxidation of the steel would also tend to minimise the decarburised zone.

The addition of CO to the neutral furnace atmosphere caused a slight decrease in the rate of scale formation with the plain carbon steels. Adding 4% of CO diminished the scaling of the low-carbon steel by roughly 10%, but this amount of CO had little effect in the presence of 0·20% of  $\text{SO}_2$ , as shown by Fig. 5. Similar results were obtained with the high-carbon steel. The presence of CO has therefore little practical value in minimising scaling losses, hence no advantages can be claimed for a furnace atmosphere obtained by incompletely burning the fuel. On the contrary, it may be stressed that such atmospheres almost invariably produce oxides which are difficult to remove from the metal either by shot-blasting or by pickling.

When a fuel is burned with excess air, the free oxygen in the resulting furnace atmosphere produces a much more severe attack on the steel; this is indicated by the appropriate curve in Fig. 5. As the free oxygen content of the furnace atmosphere rose to 2% there was a rapid increase in oxidation, but beyond this value there was little further increase. This falling-off in the effectiveness of the oxygen additions was associated with the formation of a smooth skin of ferric oxide over the otherwise brightly crystalline surface of the scale, and the latter became completely covered with ferric oxide when the free oxygen concentration in the atmosphere reached 2%.

With a furnace atmosphere containing 0·20% of  $\text{SO}_2$ , the addition of free oxygen produced an increase in scaling which reached a maximum at approximately 1% of oxygen, as shown by the upper right-hand curve in Fig. 5. Additions of oxygen beyond this value tended to inhibit the accelerating influence of the sulphur dioxide, and with the low-carbon steel the rate of scale formation in an atmosphere containing 5% of oxygen was the same whether  $\text{SO}_2$  was present or not.

The important influence of oxygen in furnace atmospheres containing  $\text{SO}_2$ , however, was to prevent the formation of iron sulphide in the scale and thus minimise intercrystalline penetration of the latter into the steel.

When the oxygen content was increased to 5% no evidence of sulphide formation could be found in the scale.

It will be clear that in dealing with sulphur-containing fuels it is not merely necessary to use more air than is required for complete combustion but sufficient to give more than 2% of oxygen in the furnace atmosphere, and from a consideration of oxide penetration it would be advisable to adjust combustion so as to give a furnace atmosphere containing 5% of oxygen.

### *Alloy Steels.*

#### *13% Manganese Steel.*

The presence of manganese in steel seems to have very little effect on either the rate of scale formation or the type of scale produced. In all the atmospheres it was found that the 13% manganese steel behaved similarly to the plain carbon steels. The effect of additions of SO<sub>2</sub> to the neutral atmosphere on the rate of scale formation is shown in Fig. 4. The results obtained in furnace atmospheres containing SO<sub>2</sub> and/or oxygen were so near those for the carbon steel that the curves shown in Fig. 5 may be taken as typical of a 13% manganese steel.

Attention is drawn to the maximum in the oxidation curve at 1% of oxygen for the furnace atmosphere containing sulphur. In this atmosphere the normal scale was covered by a dry powdery overgrowth. With higher oxygen content in the atmosphere this powdery overgrowth became less and with 5% of oxygen it finally disappeared, leaving the usual ferric-oxide-covered type of scale. The change in the appearance of the scale with increasing oxygen in the furnace atmosphere is shown in Fig. 17.

#### *5% Nickel Steel.*

In atmospheres containing no free oxygen or SO<sub>2</sub> the 5% nickel steel scaled at approximately half the rate of a carbon steel. This difference between nickel and carbon steels was less when the furnace atmosphere contained oxygen or SO<sub>2</sub>, as may be seen by comparing Figs. 5 and 6.

The nickel steel showed a higher degree of intercrystalline penetration of scale than the carbon steels. After an exposure of 1½ hr. to the neutral atmosphere containing 0·2% of SO<sub>2</sub> the penetration of scale extended to a depth of approximately 0·002 in., see Fig. 18. This atmosphere was chosen because it represents the most harmful set of furnace conditions likely to be found in practice, i.e., those obtained by the incomplete combustion of crude town gas (600 grains of sulphur per 100 cu. ft.) or fuel oil containing 3% of sulphur. The need, therefore, for using excess air in the combustion of sulphur-containing fuels for heating nickel steels is evident. The structure of the scale formed on the 5% nickel steel differed from that on the carbon steel only at the scale-metal interface, where there was a dispersion of metal particles in the inner layer of scale which was less pronounced in scales formed on the carbon steel.

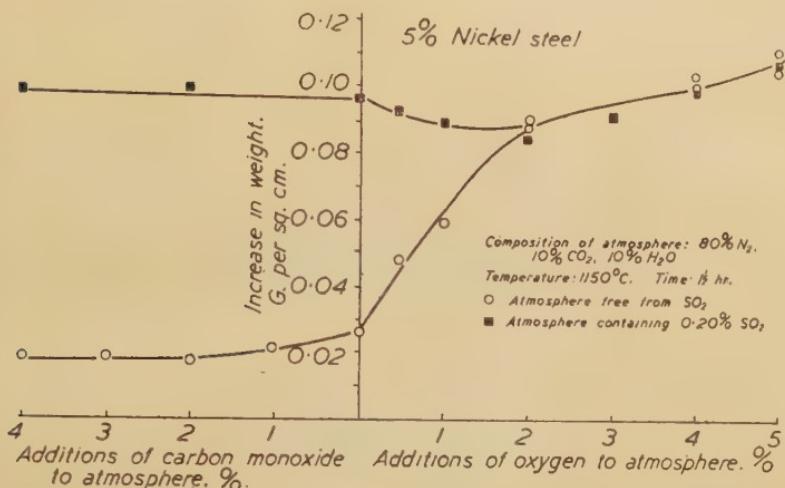


FIG. 6.—Rate of Scale Formation at 1150° C. of 5% Nickel Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

### 3.5% Nickel, 0.75% Chromium Steel.

This steel closely resembled the 5% nickel steel in its scaling characteristics in each of the furnace atmospheres. The rate of scale formation (Fig. 7) and the type of scale formed were almost the same for the two steels. There was, however, less intercrystalline penetration of the scale into the metal with the nickel-chromium

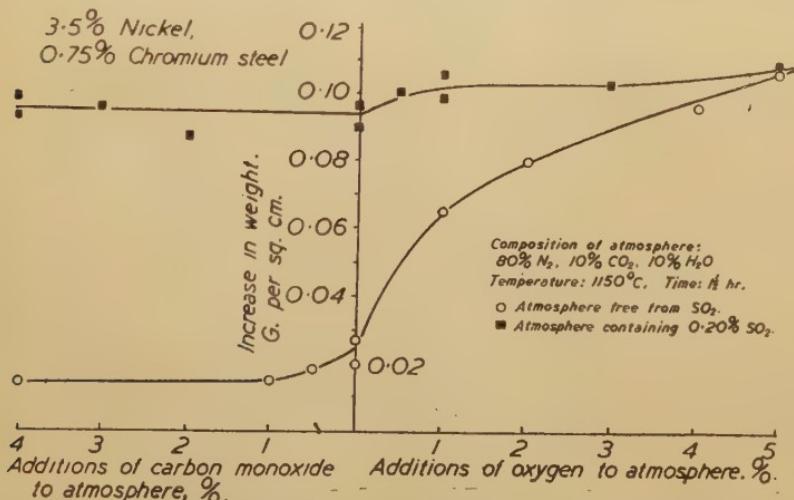


FIG. 7.—Rate of Scale Formation at 1150° C. of 3.5% Nickel, 0.75% Chromium Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

steel. There was also a finer dispersion of metal particles in the inner layer of scale.

#### 4% Silicon Steel.

In the absence of both free oxygen and  $\text{SO}_2$ , the 4% silicon steel had a comparatively low rate of oxidation, *i.e.*, approximately one-fifth of the oxidation rate of a plain carbon steel. When the furnace atmospheres contained free oxygen or  $\text{SO}_2$ , however, this superior resistance of the 4% silicon steel vanished and the rate of scale formation became greater than with the carbon steels (Fig. 8).

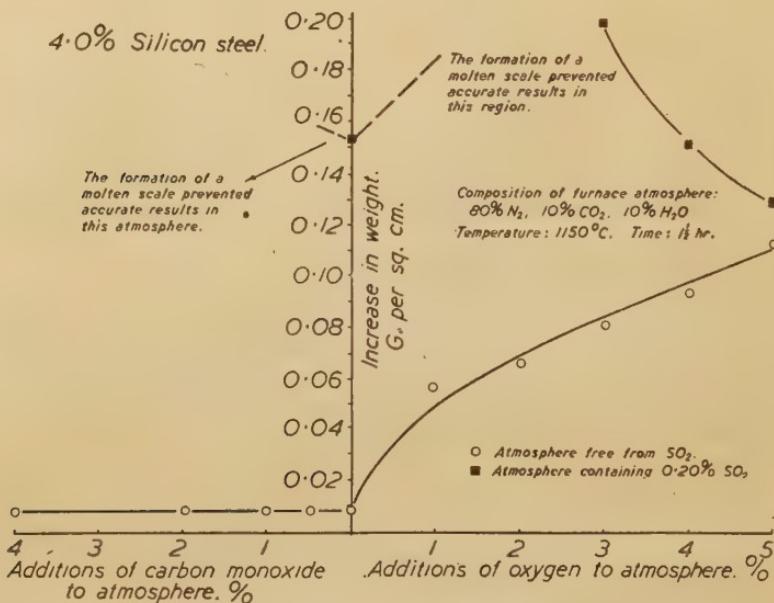


FIG. 8.—Rate of Scale Formation at  $1150^\circ \text{ C}$ . of 4.0% Silicon Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

The reason for this behaviour was revealed by the structure of the scale formed.

In the absence of both free oxygen and  $\text{SO}_2$ , *i.e.*, neutral and reducing furnace atmospheres, the scale consisted of a very thin layer of iron oxide with an inner layer of silica-rich material. The degree of resistance to oxidation possessed by this steel in such atmospheres was undoubtedly due to a low rate of diffusion of both iron and oxygen in this silica-rich layer.

When free oxygen was present in the atmosphere the inner scale layer contained another phase, which was identified as a eutectic of iron oxide and fayalite. A specimen of this eutectic was prepared by melting together 15% of  $\text{SiO}_2$  and 85% of  $\text{FeO}$ , and the

resulting structure was found to be identical with the eutectic formed in the inner scale layer of the 4% silicon steel. The equilibrium diagram of Bowen and Schairer gives the melting point of the eutectic as 1170° C., and its presence in the scale formed on the 4% silicon steel at 1150° C. can be accounted for only by assuming the presence of additional components such as iron, &c., which would lower the melting point. The greatly increased rate of scaling in the oxidising atmosphere was evidently due to the presence of this liquid phase in the scale, since only negligible traces of fayalite could be found in the scales formed when the furnace atmospheres contained no free oxygen, and under these conditions much less scaling occurred.

This liquid phase at the scale-metal interface was not accompanied by intercrystalline penetration of scale into the metal as was the case with the steels previously discussed. The absence of this penetration with the silicon steel is important, especially as this class of steel is fabricated in sheet form.

A further characteristic of this steel was the extensive decarburisation which accompanied scaling. A carbon-free zone 0.08 in. in depth was found after 1½ hr. at 1150° C. in a highly oxidising atmosphere, *i.e.*, 75% nitrogen, 10% carbon dioxide, 10% water vapour, 5% oxygen. The coarse crystalline nature of the decarburised zone is shown in Fig. 19.

Furnace atmospheres containing SO<sub>2</sub> were particularly reactive to the 4% silicon steel at this temperature, as shown by Figs. 4 and 8. The attack increased rapidly with the smallest addition of SO<sub>2</sub> to the neutral atmosphere, and 0.07% of SO<sub>2</sub> produced a type of disrupted scale similar to that formed on a carbon steel in the presence of 0.20% of SO<sub>2</sub>.

The appearance of a specimen scaled in the neutral atmosphere containing 0.20% of SO<sub>2</sub> is shown on the left of Fig. 20. The general appearance of the scale indicates that incipient fusion had occurred.

The addition of CO to this atmosphere produced a more fluid scale, which dripped from the specimen; there was also a further increase in the scaling rate. With the present apparatus it was difficult to measure accurately the rate of formation of scale when it was molten and no values are shown in Fig. 8 for this particular atmosphere.

The behaviour of the 4% silicon steel in furnace atmospheres containing both SO<sub>2</sub> and free oxygen was governed by the amount of oxygen actually present. Small additions of oxygen accelerated the rate of scaling, but above 3% the effect was negligible. Increasing the oxygen content, however, produced a more compact type of scale, as shown in Fig. 20.

The microstructure of the scale formed in the neutral atmosphere to which SO<sub>2</sub> had been added consisted chiefly of massive iron

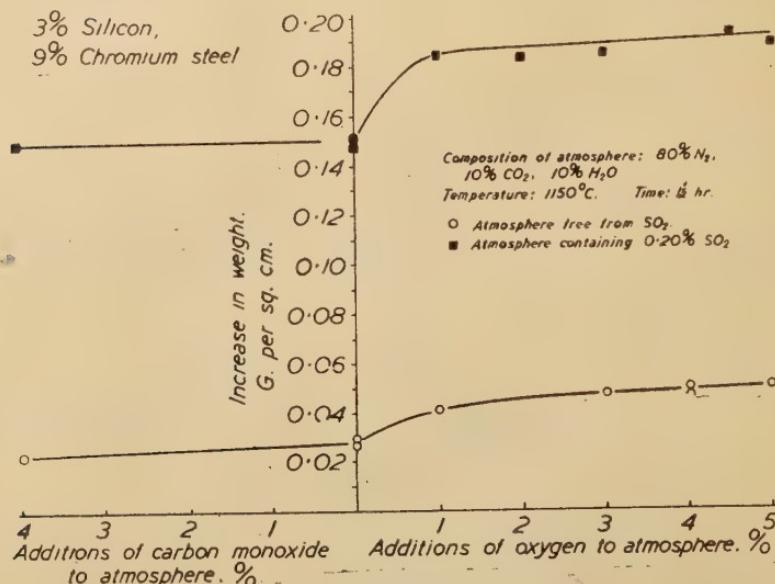


FIG. 9.—Rate of Scale Formation at 1150° C. of 3% Silicon, 9% Chromium Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

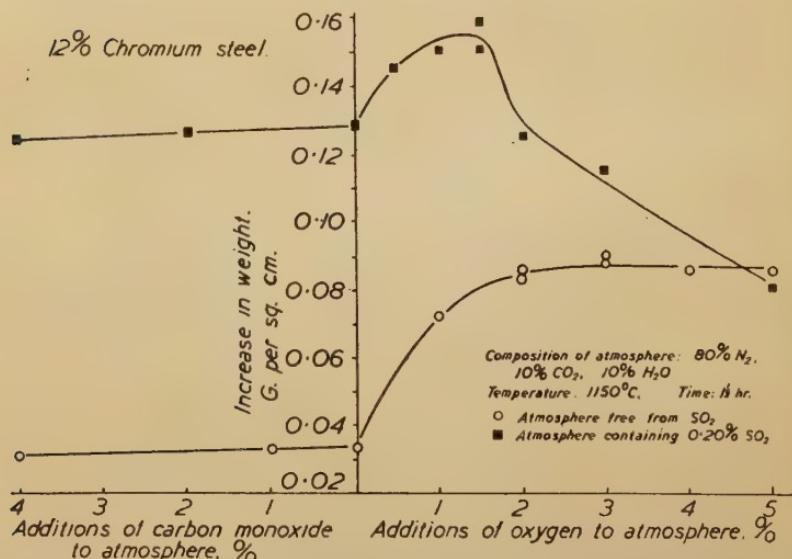


FIG. 10.—Rate of Scale Formation at 1150° C. of 12% Chromium Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

oxide with an inner layer in which two separate eutectics were visible, *i.e.*, oxide-sulphide and oxide-fayalite. These two eutectics are clearly visible in Fig. 21. Mr. J. H. Whiteley, who examined the specimen shown in Fig. 21, reported the possible presence of the ternary eutectic oxide-sulphide-fayalite. A scale containing two liquid products at the temperature of formation explains the increase in attack with the first additions of oxygen. The subsequent fall in the oxidation curve as the oxygen in the atmosphere is increased to 5% is due to a decrease in the iron-sulphide content of the scale.

The clearly defined decarburised zone found with the 4% silicon steel in sulphur-free atmospheres also occurred when sulphur was present, but there was no evidence of intercrystalline penetration of scale into the metal; this is remarkable in view of the fact that there were two liquid phases at the scale-metal interface.

### 3% Silicon, 9% Chromium Steel.

In an earlier paper<sup>(1)</sup> it was stated that at 1000° C. this steel did not readily oxidise except in high-sulphur atmospheres; a protective oxide skin formed on the steel, which became unstable only when the SO<sub>2</sub> content of the furnace atmosphere approached 0.1%. At 1150° C. there was no evidence of this protective skin, and scaling was consequently more intense, although in sulphur-free atmospheres the rate of oxidation was much lower than with the nickel, manganese or carbon steels.

Differences in the rates of scale formation between the silicon and the silicon-chromium steel may be seen by comparing Figs. 8 and 9. Unlike that on the 4% silicon steel, the scale formed on the silicon-chromium steel did not show signs of incipient fusion in the high-sulphur atmospheres, and, as the silicon content of both steels was of the same order, this higher melting point of the scale may be attributed to the presence of chromium oxide.

Decarburisation was less severe, but the scale-metal interface was not as smooth as with the silicon steel.

### Chromium, Chromium-Nickel and Chromium-Nickel-Tungsten Steels.

The results obtained with a range of chromium and chromium-nickel steels showed that the scaling characteristics are intimately bound up with the stability of the chromium-rich protective oxide film which forms on the surface of the steel immediately it is exposed to a furnace atmosphere. These films are less stable in furnace atmospheres containing SO<sub>2</sub>, but free oxygen in the atmosphere has the opposite effect.

At 1150° C. the 12% chromium steel had an appreciable rate of scale formation, especially in atmospheres containing SO<sub>2</sub>, where scaling was of the same order as with carbon steels. This may be seen by comparing Figs. 10 and 5.

In sulphur-free atmospheres at 1000° C. oxidation of this steel was limited to the formation of a green film. This film, however, had no stability at 1150° C. and normal scale formation occurred. In sulphur-free atmospheres, therefore, there is a marked difference in the scaling rate at 1000° and at 1150° C.

The scale formed at 1150° C. consisted of an outer layer of iron oxide with a complex inner layer of fine mixed oxides and metal particles. The scale-metal interface was somewhat irregular and would tend to produce an anchoring effect on the scale, making it adherent.

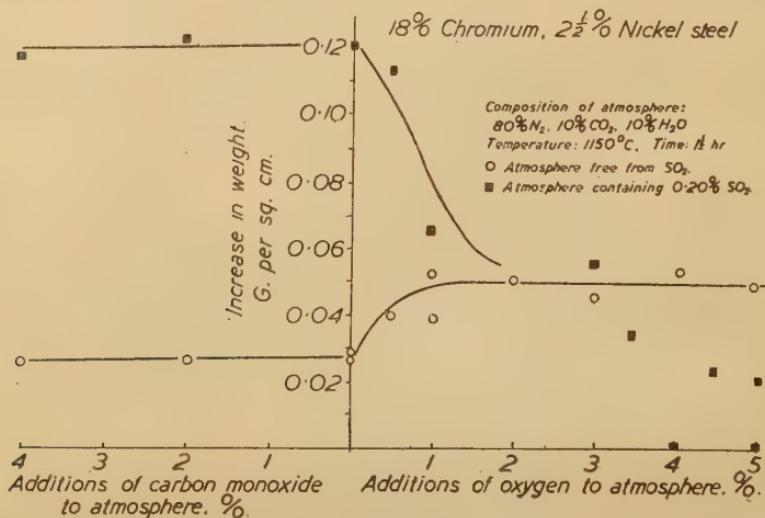


FIG. 11.—Rate of Scale Formation at 1150° C. of 18% Chromium, 2½% Nickel Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

When  $\text{SO}_2$  was present the scaling rate was greatly increased, as shown in Fig. 10, but in all cases only slight traces of iron sulphide could be detected in the scale and consequently deep intergranular penetration did not occur. An example of the complexity of the inner layer of scale is shown in Fig. 22.

Increasing the chromium content of the steel to 18% does not appear to produce any appreciable difference in scaling properties in the neutral and reducing furnace atmospheres, even when they contain  $\text{SO}_2$ . It seems that it is only in furnace atmospheres containing free oxygen that the increase in chromium content has any marked influence, and this is revealed by a tendency to strengthen the protective film. But, even so, the stability is uncertain, as is indicated by the high degree of scatter of the results shown in Fig. 11. Fig. 23 illustrates a specimen of this steel, where the chromium-rich film had broken down over part of the surface only.

The scaling properties of the 18% chromium, 8% nickel steel were also governed by the breakdown of the protective film. The addition of the nickel resulted in a lower rate of scale formation, but film breakdown seemed to be as uncertain as with the 18% chromium, 2½% nickel steel. With both these steels, when scaling did occur the structure of the scale formed was similar to that obtained with the 12% chromium steel.

This irregular type of scaling is difficult to understand and a number of experiments were made to ascertain the factors which govern the breakdown of the protective film. The results were only of a negative character, and are summarised as follows :

(1) The degree of surface finish of the steel was of little importance, but the method of grinding and polishing did seem to influence the formation of a more stable film. Vigorous grinding with appreciable heating of the specimen was more likely to give a surface which remained free from scale than careful polishing intended to avoid undue heating.

(2) Preheating in air to 600° and 1000° C. and also in the neutral atmosphere to 1000° C. so as to form complete films gave only inconclusive results.

(3) Heating the specimen slowly in the furnace atmosphere or placing the cold specimen into the furnace at 1150° C. with the atmosphere flowing through it gave no reliable information.

(4) An increase in the gas velocity over the surface of the specimen was without effect, but, on the other hand, a reduction in the gas velocity tended to secure more complete scaling.

(5) The longer the time at the scaling temperature, the more likely was the specimen to be completely covered with scale, but this scale layer was seldom of uniform thickness, indicating that failure of the film had occurred at various points on the surface of the specimen at different stages during the exposure to the furnace atmosphere.

(6) Additions of up to 5% of hydrogen to the neutral atmosphere seemed to have no effect on the stability of the film.

(7) Giving the specimen a high electrical potential, both positive and negative in turn, and also maintaining a high-voltage discharge through the furnace atmosphere were all without effect on the stability of the film.

The above results, whilst inconclusive, would suggest that this uncertainty in the stability of the protective film may be associated with a condition of the specimen rather than with the furnace atmosphere.

In experimenting with more highly alloyed steels such as a 20% chromium, 7% nickel, 4% tungsten, a 25% chromium, 17% nickel, and a 30% chromium steel, it became clear that an increase in the chromium and nickel content resulted in a more stable protective film.

*8% Aluminium Steel.*

In atmospheres free from  $\text{SO}_2$  and oxygen, oxidation was confined to the formation of a thin film which underwent very restricted breakdown at points on the surface to give small black crystals of scale, as shown in Fig. 24. Additions of oxygen to the sulphur-free furnace atmosphere produced a greater number of isolated patches of scale, Fig. 25.

The values plotted in Fig. 12 illustrate the degree of variability in the breakdown of the alumina-rich protective film in furnace

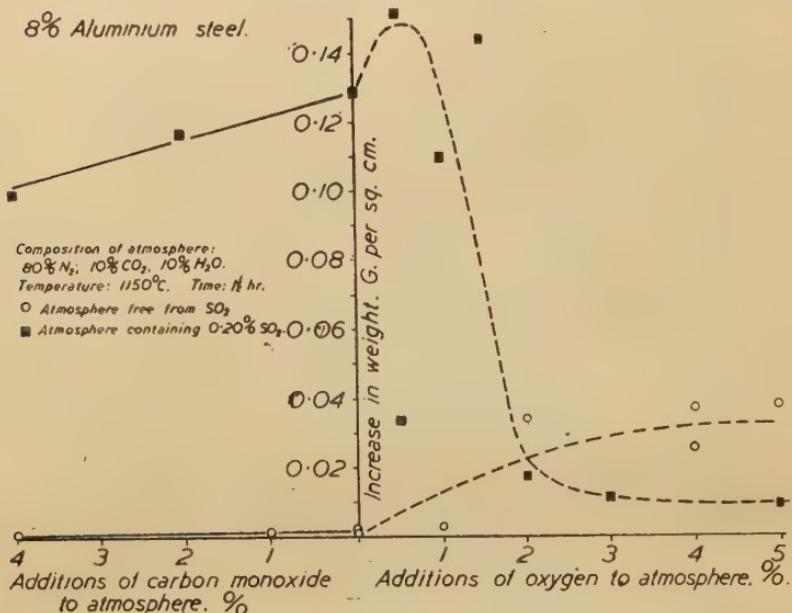


FIG. 12.—Rate of Scale Formation at 1150° C. of 8% Aluminium Steel in Furnace Atmospheres containing Carbon Monoxide or Oxygen, respectively.

atmospheres containing oxygen and  $\text{SO}_2$ . In sulphur-containing atmospheres, with low oxygen contents the rate of scale formation which followed the failure of the protective film was as high as with the carbon steel.

The scale formed in sulphur-containing atmospheres consisted of three zones :

- (1) An outer layer of massive iron oxide.
- (2) A complex inner layer.
- (3) A modified surface zone in the metal beneath the scale.

The complex inner layer consisted of a ground-mass of iron oxide in which well-defined crystals of alumina and minute grains of metal occurred, as shown in Fig. 26. The modified metal surface

contained filaments of scale which penetrated to a depth of approximately 0·015 in. This modified layer is shown in Figs. 27 and 28.

It may be mentioned that among attempts to produce by some pretreatment a stabilised alumina-rich film which would resist attack by furnace atmospheres at 1150° C., the M.B.V.\* process was tried, but was not successful.

### CONCLUSIONS.

The results obtained in an examination of the scaling properties of steels at 1150° C. may be summarised as follows.

The composition of the furnace atmosphere, especially with regard to its SO<sub>2</sub> and oxygen contents, is an important factor in controlling the scaling properties of steels exposed to it.

Apart from the alloy steels containing chromium, aluminium or silicon, no difference was found in the scaling characteristics at 1000° and 1150° C., except for a large increase in the actual rate of attack. With the chromium, aluminium or silicon steels, continued oxidation was dependent upon the failure of a protective oxide film which formed in the early stages, and these protective films were less stable at 1150° than at 1000° C.

The presence of SO<sub>2</sub> in the furnace atmosphere was associated with the following scaling characteristics :

- (1) Increased rate of scaling.
- (2) Increased tendency for breakdown of the protective film with chromium, aluminium and silicon steels.
- (3) Intercrystalline penetration of the scale in varying degree, with the exception of chromium, aluminium and silicon steels, where it did not occur.

Oxygen in the furnace atmosphere very largely counteracted the effect of the SO<sub>2</sub> and also produced a less adherent type of scale.

With certain steels (carbon, 13% manganese, 12% chromium and 4% silicon) the presence of small percentages of oxygen, *i.e.*, up to 2%, accentuated the effect of the SO<sub>2</sub>, and in most cases it was necessary to have 4% or 5% before the influence of the SO<sub>2</sub> was completely nullified.

The scaling properties of 13% manganese steel were, for all practical purposes, identical with those of a carbon steel.

A 5% nickel steel gave a lower rate of scale formation than the carbon steel, but the intercrystalline penetration of scale into the metal was more intense.

An oil-hardening nickel-chromium steel (3½% nickel, ¾% chromium) behaved like the 5% nickel steel except that there was less intercrystalline penetration of scale in atmospheres containing sulphur.

\* Boiling in a solution of chromic acid.

The oxidation of a 4% silicon steel was characterised by the formation of liquid silicate at the scale-metal interface in atmospheres containing free oxygen. When  $\text{SO}_2$  was also present a second molten phase (oxide-sulphide complex) was formed. These molten phases produced a high rate of scale formation, but there was no intercrystalline penetration of the scale. Decarburisation of the metal beneath the scale was another important feature of the oxidation of this steel, and the decarburised zone was coarsely crystalline.

The scaling properties of high-chromium and chromium-nickel steels are intimately bound up with the relative stability of the protective oxide film. Increasing the chromium and, to a lesser degree, the nickel content seems to result in an increase in the stability of this film.

In a like manner the behaviour of an 8% aluminium steel was also governed by the properties of an alumina-rich protective film, which prevented further oxidation of the steel. Fairly rapid oxidation of the steel occurred when the protective film broke down.

#### ACKNOWLEDGMENTS.

The authors wish to thank members of the Alloy Steels Research Committee for their continued support of this work. They would thank also Dr. Jenkin for his personal interest and Professor Townsend for granting facilities for the experimental work involved in this investigation.

#### REFERENCES.

- (1) A. PREECE, G. T. RICHARDSON, E. SIMISTER and J. W. COBB : Second Report of the Alloy Steels Research Committee, Section III., p. 9, *The Iron and Steel Institute*, 1939, *Special Report No. 24*.
- (2) W. H. HATFIELD : *Journal of the Institute of Fuel*, 1938, vol. 11, Apr., p. 245.
- (3) A. PREECE, G. T. RICHARDSON and J. W. COBB : First Report of the Alloy Steels Research Committee, Section XI., p. 215, *The Iron and Steel Institute*, 1936, *Special Report No. 14*.

#### CORRESPONDENCE.

Dr. T. P. HOAR (Metallurgical Laboratories, Cambridge) wrote : This paper is a welcome extension of the previous reports from the same laboratories. The great accelerating influence of factors leading to scale that is liquid at the temperature of its formation, and the considerable retarding influence of the alloying elements aluminium, silicon and chromium, *provided* that the scale being formed is solid, are strikingly shown. These new high-temperature facts, as well as being of great interest from the practical point of view,

give further support to the general physico-chemical theories of the interaction of metals with gases.

I think it would be desirable if the authors would give us a little more information on one or two points concerned with the data recorded in Fig. 4. First, for the high-carbon steel in the neutral atmosphere the diagram shows a lower weight increase, some 30% only of the weight increase with the low-carbon steel. Is this due entirely to greater loss of carbon from the high-carbon steel? The authors report only net weight increases in this paper, and do not give results for the carbon loss similar to those reported in the earlier work; if any are available, it would be of interest to have them, for comparison with the lower-temperature results. Secondly, Fig. 4 is evidently a revised version of Fig. 17 in the earlier paper,<sup>1</sup> and, apart from additional data, it contains several notable changes—in particular, the first two points on the 4% silicon curve, and the first point on the 12% chromium curve—all of which indicate much smaller weight increases than the points they replace. It is probably improvements in experimental technique that have led the authors to make these changes, but in view of the practical and theoretical importance of the relative rates of scaling of plain, silicon and chromium steels, it would be of interest if they would tell us the complete reasons for the revision.

Mr. ROOSEVELT GRIFFITHS (University College of Swansea) wrote: A word of caution should be added to the statement on the second page that the size and shape of the specimen does not appreciably affect the figure for the increase in weight per unit area. Whilst this may be true for the size and shape of specimens tested by the authors, it certainly does not hold where the diameter of the specimen is small, as in wire specimens or where the decrease in metallic diameter resulting from oxidation is excessive—in other words, where the area of the metal/scale interface decreases rapidly with oxidation. This factor may upset the comparison of results.

With regard to the high degree of scatter of the results found with the chromium and chromium-nickel steels, there is no doubt that this is due to blistering of the scale, as can be seen from Fig. 23. There is no doubt, judging from Fig. 17, that this effect is present with the 13% manganese steel when less than 1% of oxygen is present in the neutral atmosphere. Local separation of the scale from the steel surface takes place, followed by sintering of the blister formed, which may eventually fall off as a powder. The blistering of scale was investigated by the writer and was the subject of a paper to the Institute.<sup>2</sup> There is a possibility that blistering was aggravated in the authors' specimens by the forged

<sup>1</sup> Preece, Richardson and Cobb, Second Report of the Alloy Steels Research Committee, p. 52, *The Iron and Steel Institute*, 1939, Special Report No. 24.

<sup>2</sup> *Journal of The Iron and Steel Institute*, 1934, No. II., p. 377.

or rolled conditions of the steel. Annealing for a sufficient time to remove the strains before oxidation is commenced is necessary; the heating period up to the oxidation temperature is often not sufficiently long. Where blistering occurs the figures for the results of the degree of oxidation can, under certain circumstances, vary twofold and more, and the only way to obtain an estimate of the rate of oxidation is by a statistical analysis from a number of determinations. I would be interested to know the number of specimens used by the authors for each determination and how closely their values agreed.

The authors' method of supporting the specimens in the furnace could be improved by, say, drilling a hole through the specimen from the centre of the flat face and suspending the specimen on a wire fitting tightly in this hole. In the authors' method there might be a variation in area of contact between the wire supports and the specimen and also a masking effect of the wires which sets up a shadow effect when the gases sweep past the specimen.

#### AUTHORS' REPLY.

The AUTHORS wrote in reply : We thank Dr. Hoar for drawing attention to the statement in the text regarding the relative scaling rate of the two carbon steels. In the neutral atmosphere the rate of oxidation of the 1.3% carbon steel was approximately half the rate found with the 0.13% carbon steel, as shown by the following results :

Atmosphere 80% N<sub>2</sub>, 10% CO<sub>2</sub>, 10% H<sub>2</sub>O. Temp. 1150° C.

Time of exposure 1½ hr.

Weight of scale formed on { 0.13% carbon steel = 0.19 g. per sq. cm.  
1.3% " " = 0.10 " " "

We did not include figures for carbon loss in the present paper, since this subject will be treated fully in a later one on the decarburisation of steels in furnace atmospheres which it is hoped will be published in the near future.

With regard to Dr. Hoar's second point, the results quoted in the two papers were obtained by different workers using different types of furnaces. The agreement in the results obtained was very satisfactory, except in one or two instances where the lower results given in the later paper were obtained by taking special precautions to avoid sulphur contamination from furnace tubes that had been previously used for sulphur-containing atmospheres. Great difficulty was experienced in removing a black deposit which formed on the inside of the furnace tube during the oxidation of the steel in furnace atmospheres containing sulphur dioxide and little or no free oxygen. The higher results in the earlier paper were thought

to be due to traces of sulphur remaining in the furnace tube from a previous experiment.

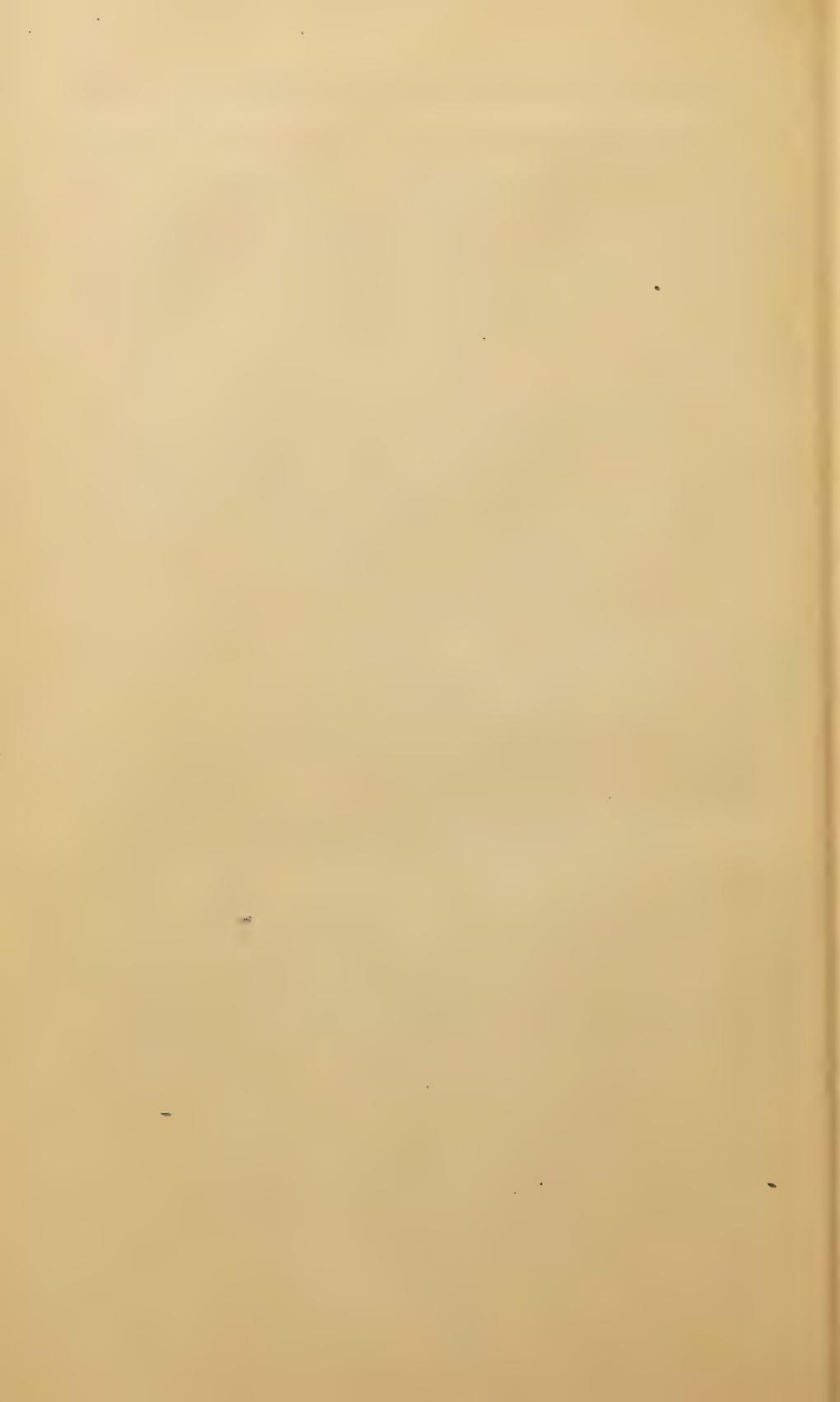
We agree with Mr. Griffiths that with thin wires there would, no doubt, be a limiting condition where, during oxidation, the change in area of the metal/oxide interface would have to be taken into consideration. We would like to stress, however, that our intention in carrying out tests on specimens of different size and shape was to demonstrate that with the specimens used in the present investigation and consequently with larger masses these factors, together with "corner effects," &c., were of negligible importance.

The high degree of scatter quoted for the high-chromium and chromium-nickel steels could not be attributed to the blistering of scale. We have obtained ample evidence to show that the scatter referred to was due to a variation in the life of the protective oxide which formed on the specimen during the initial stages of oxidation. Further, it may be stated that many of the specimens showed no signs of blister formation, yet the difference in degree of oxidation was as great as with those where the scale had formed blisters.

The number of check tests for each determination varied with the circumstances. Generally speaking, in atmospheres giving relatively low rates of oxidation the experimental error was  $\pm 5\%$ . With atmospheres giving higher scaling rates this error was less. Duplicates were expected to agree well within this range and any results outside this limit were further examined. Where a series of results could be plotted on a smooth curve single tests were made, and any results which did not fall reasonably near the curve finally obtained were repeated.

Experimental results are given in all the figures so as to indicate clearly the general agreement or divergence obtained.

We prefer the simple method of supporting the specimens in a platinum-wire cradle to that suggested by Mr. Griffiths. The area of contact between the wire and the specimen was too small to have any measurable effect on the results obtained. This was demonstrated indirectly by obtaining a similar figure for the oxidation rate in the series of tests with specimens of different size and shape. The agreement obtained in this series of tests would also, in our opinion, dispose of any doubts regarding the possibility of introducing errors due to the shadow effects mentioned by Mr. Griffiths.



# CLEANING AND DESCALING STEEL BY ELECTROLYTIC PICKLING IN MOLTEN CAUSTIC SODA.\*

BY N. L. EVANS, B.Sc., A.I.C. (RESEARCH DEPARTMENT, I.C.I. (ALKALI), LTD., NORTHWICH, CHESHIRE).

(Figs. 5 to 13 = Plates XIV. to XVII.)

## SUMMARY.

It is claimed for the process of cleaning and descaling steel by electrolytic treatment in molten caustic soda that it produces a highly satisfactory surface for subsequent operations such as plating, galvanising, tinning, vitreous enamelling, painting, &c. It imparts to the steel a mild degree of resistance to rusting, and hydrogen is not absorbed as in certain other scale-removal methods. Metallic losses are minimised and the consumption of chemicals is low.

The present investigation is concerned mainly with finding the optimum conditions of time, temperature and current density, and with the occurrence and prevention of brown stains on the work. Certain electrical conditions in the plant have been investigated, and their bearing on plant design is discussed. Several other matters relating to the plant are dealt with, including precautions necessary for safe operation, methods of removing sponge iron from the treated metal surfaces, methods of heating the caustic soda, and the method of collecting and removing sludge from the tanks.

## I.—INTRODUCTION.

THIS paper deals with certain aspects of a process for the electrolytic pickling of steel in molten caustic soda.

In 1936, a British patent (No. 442,859) was granted for a process for cleaning and descaling metal by electrolytic action in a bath of molten caustic soda. The specification mentions other chemicals for the bath, such as mixtures of sodium and potassium hydroxides, sodium nitrite and calcium chloride, but, so far as the author is aware, caustic soda has invariably been used when the process has been applied in Great Britain. Suitable operating conditions are said to be a temperature of 850° F. (454.5° C.), a current density of 100 amp. per sq. ft. and an immersion time of 10–15 sec. The metal to be cleaned is made the cathode, the anodes being of nickel or iron. The consumption of caustic soda is said to be 15 lb. per ton in the case of wire.

The advantages claimed<sup>(1)</sup> for the process are as follows :

(1) It produces a cleaner and more uniform surface than can be obtained by other methods, and consequently allows the production of better coatings, whether the steel is to be plated, tinned, enamelled, painted or otherwise treated.

\* Received August 13, 1943.

(2) The consumption of chemicals is small.

(3) The process avoids the loss of weight which the steel undergoes in acid pickling. This may be an important factor when expensive alloys are involved.

(4) The nature of the process precludes the possibility of embrittlement of the steel through absorption of hydrogen.

(5) By the use of appropriate salts and proper temperatures the steel may be given heat treatment, such as annealing, tempering, &c., at the same time as it is being cleaned.

(6) The process completely cleans metal surfaces from all organic material, so that no preliminary degreasing step is necessary.

(7) The process can be used in place of sand-blasting in nearly all cases; it is particularly effective as a preliminary to inspection to show defects in welds, castings, &c.

(8) Steel cleaned by this process may be stored, transported, &c., without the rusting which occurs immediately after acid pickling. This makes it unnecessary to do the pickling immediately before the article is to be coated, permitting simplification of manufacturing plant flow sheets.

The process was first developed as a method of cleaning steel wire prior to electro-galvanising. Lyons<sup>(2)</sup> has described the extreme difficulty of removing from steel wire the surface contamination resulting from the application of drawing compounds followed by the passage of the metal through dies, which raises the surface temperature momentarily to a high value. He considers that pickling in acid is inadequate for removing the resulting deposits, but that the caustic soda process produces a surface sufficiently clean for electro-galvanising. This method was developed by the Bethlehem Steel Corporation, the combined processes of cleaning and zinc-plating being known as "bethanising."

Hammell<sup>(3)</sup> refers to the claims made for the process that it removes oil, dirt, scale, carbon and phosphorus from steel surfaces, and remarks that metal so treated should have less tendency to rust if stored than metal cleaned by other means. He experimented with the vitreous enamelling of sheets after cleaning by this method, and found with certain higher-carbon steels a better adherence of the coating than was obtained after acid pickling. He noted a slight etching of the surface in the case of higher-carbon steels, but it was not so marked as the etching produced by acid pickling. He gives as the conditions of carrying out the process, a bath of molten caustic soda at 500° C. contained in a steel tank, nickel anodes, 6-V. direct current, a current density of 2-2½ amp. per sq. in. (288-360 amp. per sq. ft.) and an immersion time of 1½-2 min., followed by washing in hot caustic solution and then in hot water.

There are literature references<sup>(4)</sup> to electro-galvanising with a

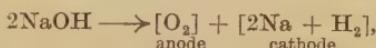
specially pure grade of zinc (99.995%), which is claimed to possess definite advantages over the usual 99.95% grade. It is possible to apply a coating of 3 oz. per sq. ft. on pure iron wire, which can then be wrapped around its own diameter without cracking. Electro-galvanised wire originally coated with 4 or 5 oz. of zinc per sq. ft. can be drawn down to a smaller diameter, and it is possible in the case of sheet steel to put, say, 2 oz. of zinc per sq. ft. on one side, and  $\frac{1}{2}$  oz. on the other. An essential preliminary is the perfect cleaning of the steel by electrolysis in molten caustic soda. There are other applications of this method of cleaning, such as the manufacture of aircraft bearings and the production of stainless-steel rods, and it is claimed that in all cases it does a better and faster job, and often a much cheaper one.

The bethanising process has been extensively used in Great Britain for the production of galvanised steel wire. More recently, experiments have been carried out on a fairly large scale on the descaling of steel sheet by the caustic-soda process, not as a preliminary to galvanising but as a final treatment which confers a mild degree of resistance to rusting for an appreciable period, in contrast to the rapid rusting which follows pickling in acid.

The main object of the present investigation was to find the most favourable conditions of temperature, time and current density for carrying out the process. In the course of the investigation a considerable amount of information has been collected on such subjects as the design of plant, safety precautions, the descaling of certain alloy steels, and suchlike, and it is felt that this may with advantage be recorded for users and potential users of the process.

## II.—MECHANISM OF PICKLING IN MOLTEN CAUSTIC SODA.

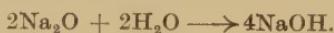
The basic chemical reactions on which the process depends are probably (a) the electrolysis of caustic soda, or some other suitable sodium compound, to produce sodium metal :



(b) the reduction of iron oxide at the cathode by sodium :



and (c) the re-formation of sodium hydroxide :



The iron which forms as a result of reaction (b) may remain on the parent metal as a fine powder, or it may come away and form a sludge. If it is washed and allowed to dry while adhering to the original sheet it may be readily peeled off in the form of foil. Fig. 5 shows some pieces of this reduced iron foil, the thickness varying from 0.001 to 0.0025 in. Fig. 6(a) is an X-ray photograph of

reduced iron washed off some descaled sheet with water. The lines are characteristic of metallic iron. The sludge which collects in the bottom of the vessel has the appearance of a thick, almost black mud, slightly tinged with brown. On cooling, it sets into a hard, brick-coloured mass, one sample of which had the following analysis :

Caustic soda . . . . .	80.52%
Sodium carbonate . . . . .	4.96%
Iron . . . . .	15.41%
Silica . . . . .	0.45%
Lead . . . . .	4.08%

An X-ray photograph of this (Fig. 6(b), middle) shows that the iron is present as sodium ferrite ( $\text{NaFeO}_2$ ). Standard photographs of sodium hydroxide and sodium ferrite are also shown to establish identification.

The commercial grade of flake caustic soda is suitable for this process. A typical analysis is :

$\text{Na}_2\text{O}, 76.56\%$					
$\text{NaOH}$ . . . . .	98.33%	$\text{SiO}_2$ . . . . .	0.30%		
$\text{Na}_2\text{CO}_3$ . . . . .	0.64%	$\text{CaO}$ and $\text{MgO}$ . . . . .	0.014%		
$\text{NaCl}$ . . . . .	0.26%	$\text{Fe}_2\text{O}_3$ . . . . .	0.0014%		
$\text{Na}_2\text{SO}_4$ . . . . .	0.59%	$\text{Al}_2\text{O}_3$ . . . . .	0.0024%		

### III.—DESCRIPTION OF LABORATORY EXPERIMENTS.

#### (1) *The Cell Installation.*

The apparatus as set up at the commencement of the investigation consisted of a rectangular mild-steel cell with welded seams. The metal was  $\frac{1}{4}$  in. thick and the outside dimensions were : Length 9 in., width 5 in. and depth 9 in.

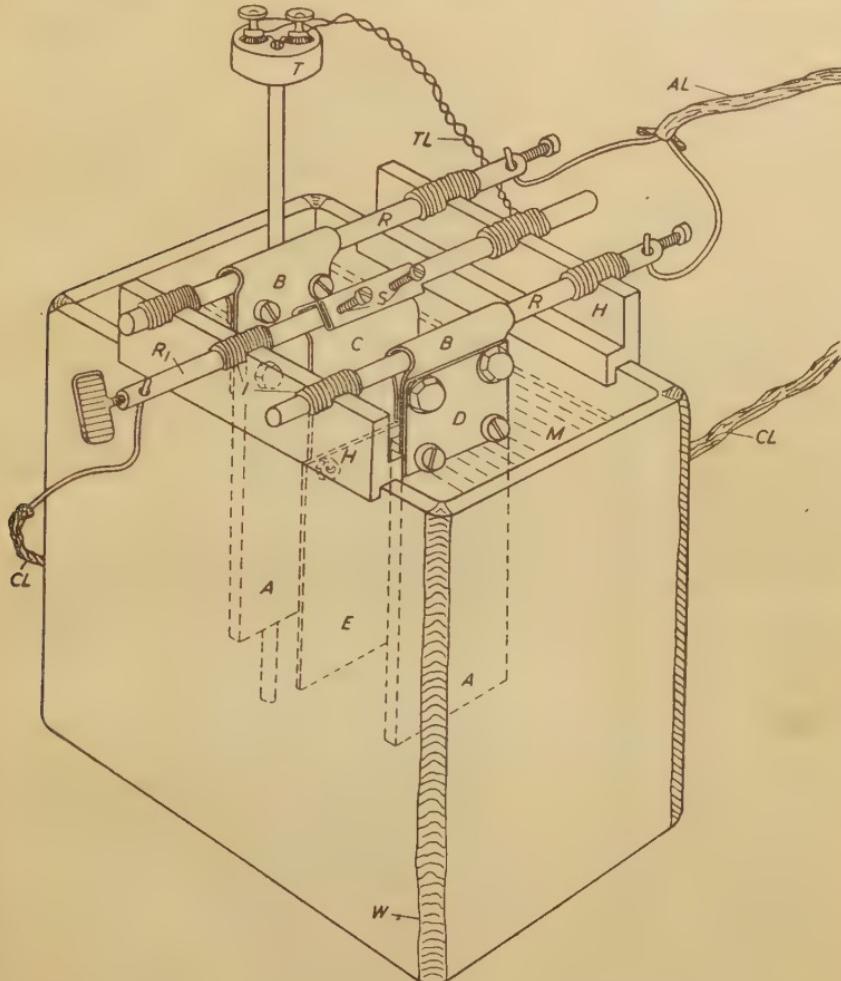
The four sides of the cell were lagged with  $\frac{1}{4}$ -in. thick asbestos sheet bound with wire. Two grooved strips of an insulating material, "Sindanyo," were placed along the broader edges of the cell and opposite to each other. These served to carry and to insulate from each other the two outer nickel anode plates *A*, and, in the centre between them, the cathode connection *C* (see Fig. 1).

The nickel anode plates were bolted to and suspended from the  $\frac{1}{2}$ -in. dia. copper conductor rods *R* by means of a looped wide strip of copper. The cathode connector *C* consisted of a strip of nickel, 3-mm. thick and  $1\frac{1}{2}$  in. wide, secured to give good electrical connection to the copper conductor rod *R*<sub>1</sub> by means of two tangentially placed set-screws *S*. The cathode connector was drilled  $\frac{1}{4}$  in. at two points 1 in. apart at its lower end and the test strip of steel was similarly drilled and fastened to the connector by  $\frac{3}{16}$ -in. dia. short bolts and nuts.

The test strips of the various steels tried were generally cut to a length of 4 in. and a width of 1.8 in., thus giving a convenient total surface area of one-tenth of a square foot.

With the aim of increasing the safety of operation, the free

space in the cell was covered by means of a rectangular "Sindanyo" plate,  $\frac{5}{8}$  in. thick, widely slotted in three places to allow



R.—Anode Conductor Rods. R<sub>1</sub>.—Cathode Conductor Rod. B.—Bent Strip Connectors. C.—Nickel Cathode-Holder. I.—Asbestos-String Insulators. H.—Steel Carrier Bars. T.—Thermocouple. AL.—Asbestos-covered Anode Lead. CL.—Asbestos-covered Cathode Lead. S.—Setscrews securing Cathode-Holder. M.—Molten Caustic Electrolyte Surface. W.—Welded Seam of Mild-Steel Cell. D.—Distance Piece bolted to Nickel Anode. TL.—Thermocouple Leads. A.—Heavy Nickel Anode Plates E.—Steel Test Strip.

FIG. 1.—The Experimental Pickling Cell.

the anodes and cathode connector to be passed through. This was later removed (see paragraph 5 below). A small hole was also provided in the cover to admit the nickel tube containing the

thermocouple which registered the temperature of the electrolyte. The chromel-alumel thermocouple was connected to a millivoltmeter through chromel and alumel leads. The cell thus fitted was housed behind a glass screen. Heating of the bath was effected by means of two Meker burners placed beneath it.

The current supply consisted of a 110-V., D.C. generator fitted with a rheostat in the field winding which permitted the voltage to be reduced to values of from 2 to 4 V. as required to maintain the operating current of 100 amp. and upwards per sq. ft. Asbestos-covered heavy leads carried the current to the binding screws fitted to the ends of the conductor rods. A voltmeter and an ammeter completed the equipment.

### (2) Charging and Operation.

Flake caustic soda was put into the open cell with the electrodes removed. Both Meker burners were lighted, and in the course of 2½ hr. the cell was full to within 2 in. of the top with molten caustic soda, the alkali being added at intervals. The slotted cover was then fitted and the two anodes and the cathode holder were introduced and wired to their leads.

Displacement raised the caustic level to about 1½ in. from the top of the cell, just sufficient to submerge the trial strips.

When once charged with molten caustic soda the cell was maintained in this condition continuously for periods of up to two weeks. Solidification and remelting of the charge from day to day is to be deprecated, since it imposes stresses on the cell and a risk of expulsion of molten caustic soda during melting.

Having bolted the test strip to the cathode holder, they were carefully lowered into the electrolyte and the cathode lead was attached. The current was then switched on and adjusted to the required value. The treatment was continued for the time required; the current was then cut off and the cathode lead detached. Using tongs, the holder and test-piece were immediately withdrawn and plunged into a bath of cold water. The test-piece was then seen to be covered with a grey-black film of finely divided sponge iron. It was next immersed in a vessel containing boiling water and vigorously brushed on both surfaces. If the treatment had been adequate the whole of the oxide film was converted to sponge iron, which was easily removed by this treatment. A final swill in boiling water left the work bright and clean, and, after drying, the piece was unbolted and the operation repeated with a new piece.

It was found desirable to apply graphite to the securing bolts of the test-pieces to aid the removal of the nuts.

### (3) Preliminary Work to Establish Broad Principles of Operation.

A number of samples of miscellaneous ferrous metals were treated in the molten caustic soda bath. The conditions of the tests and the results are set out in Table I. Many of the specimens were of



FIG. 5.—Reduced Iron Foil, stripped from sheet of electrolytic descaled steel.  $\times \frac{1}{3}$ .

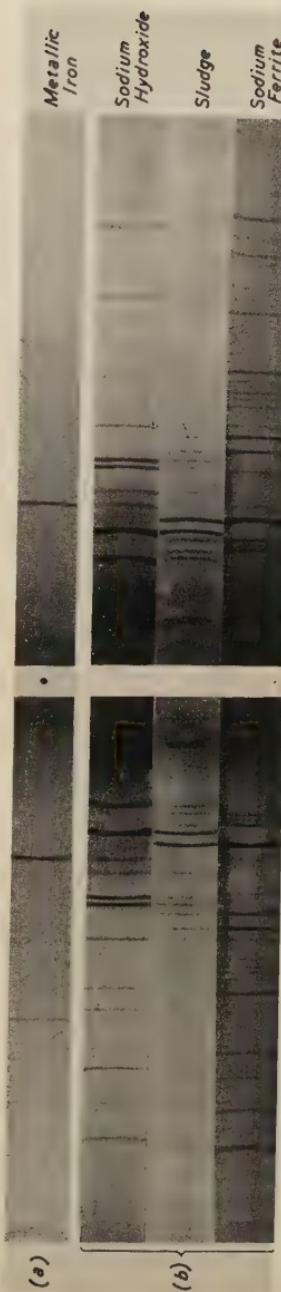


FIG. 6.—(a) X-Ray Spectrogram of Reduced Iron, washed off descaled steel sheet. (b) Spectrogram of Sludge from an Electrolytic Pickling Tank (centre), with comparative spectrograms of sodium hydroxide (above) and sodium ferrite (below).

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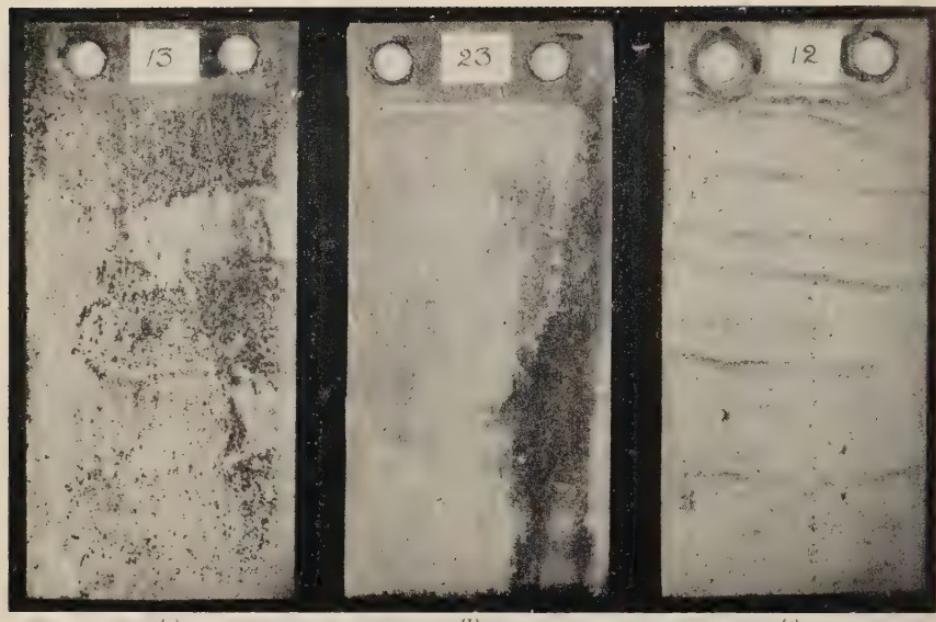


FIG. 7.—Types of Brown Stain. (a) Stain associated with a pitted surface and insufficient pickling. (b) Type A stain. (c) "Water-mark" stain, type F.

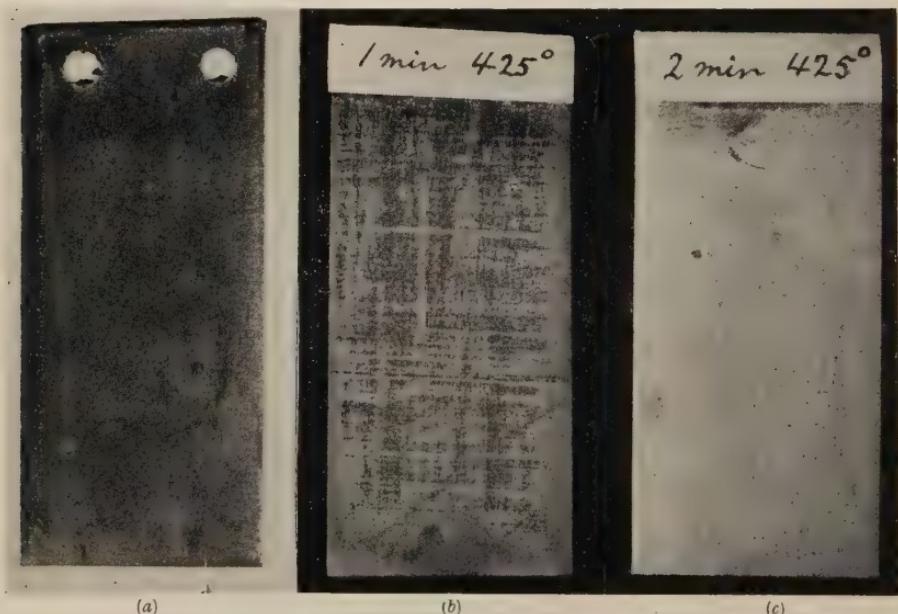


FIG. 8.—Mild Steel (No. 2), with moderately thick smooth blue rolling-mill scale. (a) Untreated. (b) Partly descaled; 1 min., 425° C., 100 amp. per sq. ft. (c) Fully descaled; 2 min., 425° C., 100 amp. per sq. ft.

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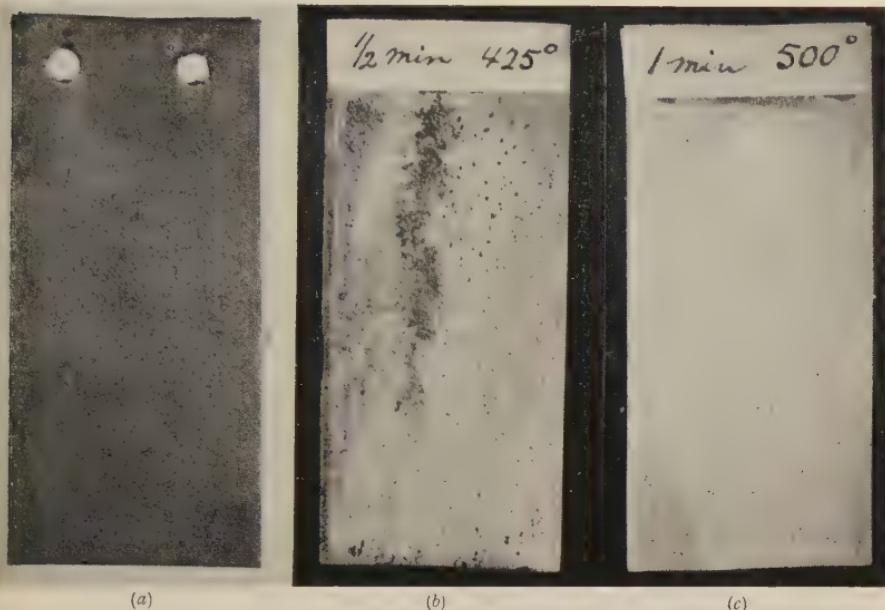


FIG. 9.—Mild Steel (No. 3), with moderately thick dull blue scale. (a) Untreated;  $\frac{1}{2}$  min., 425° C., 200 amp. per sq. ft. (b) Partly descaled; 1 min., 500° C., 200 amp. per sq. ft.

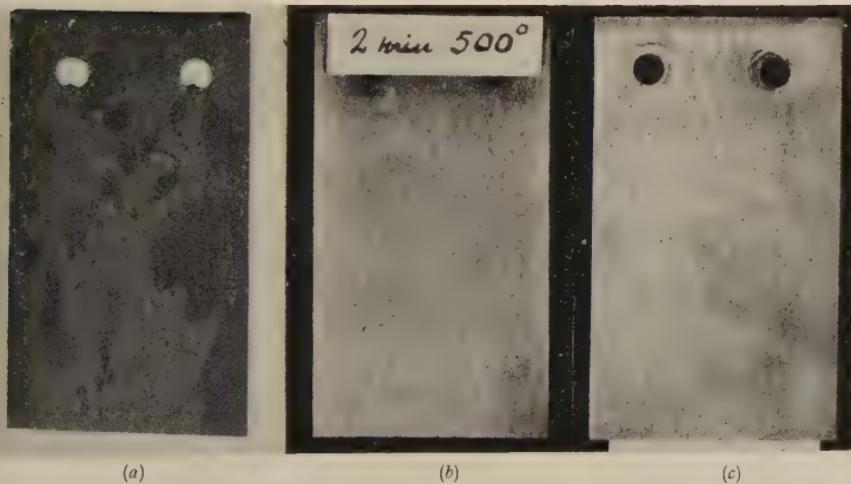


FIG. 10.—Cutlery-Type 12-14% Chromium Stainless Steel (No. 18). (a) Untreated. (b) 2 min., 500° C., 200 amp. per sq. ft. (c) 4 min., 500° C., 200 amp. per sq. ft.

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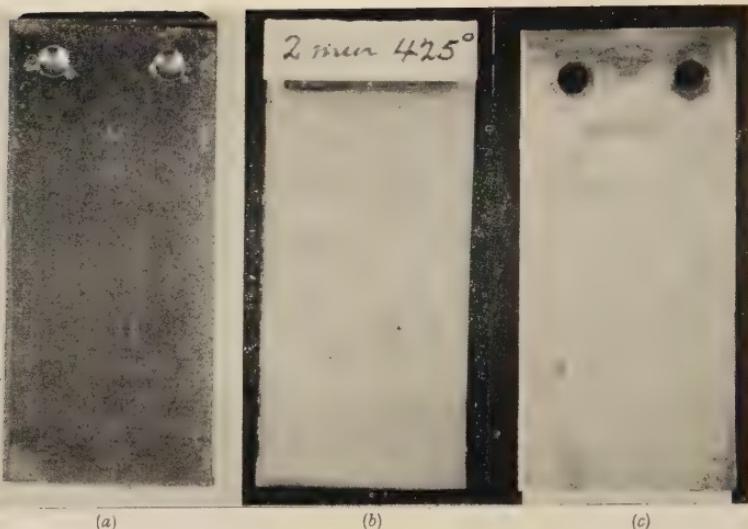


FIG. 11.—S80 Stainless Steel (No. 12). (a) Untreated. (b) Fully descaled; 2 min., 425° C., 100 amp. per sq. ft. (c) Fully descaled; 4 min., 500° C., 200 amp. per sq. ft.

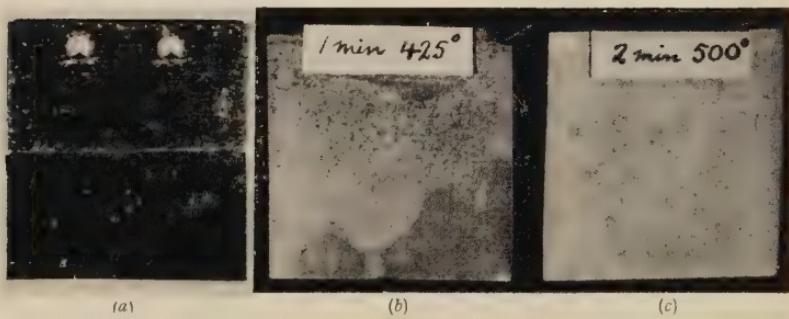


FIG. 12.—0.25% Silicon Steel (No. 24), hard rolled. (a) Untreated (showing both sides). (b) Partly descaled, some brown stain; 1 min., 425° C., 100 amp. per sq. ft. (c) Fully descaled, some brown stain; 2 min., 500° C., 200 amp. per sq. ft.

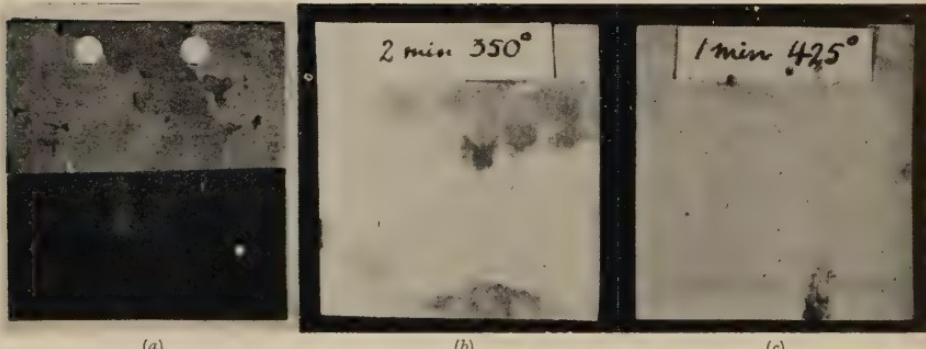


FIG. 13.—4% Silicon Steel (No. 21), close-annealed. (a) Untreated (showing both sides). (b) Fully descaled, but with brown stain; 2 min., 350° C., 100 amp. per sq. ft. (c) Fully descaled; 1 min., 425° C., 200 amp. per sq. ft.

TABLE I.—Record of Preliminary Experiments.

Experiment No.	Description.	Temp. of Caustic, ° C.	Time, Min.	Current Conditions.	Total Surface Area, Sq. in.	Current Density Amp. per sq. ft.	Remarks.	
				Amp.	V.			
1	Rusty steel sheet*	{ 365 365 365	5 2 35	25.5 40 5	4 5.3 7.5	7.5 5.7 7.5	All rust removed. Grey deposit on surface easily washed off by hot water jet.	
2								
3								
4	Rusty steel sheet	{ 350 340 345 345 345	2 5 5 10	20 4.25 4.5 3.75	8 8 8 8	360 360 360 180	Rust removed but a brown stain remained. Rubbing appeared to remove some sponge iron.	
5								
6								
7								
8								
9	Rusty steel plate, irregular shape, $\frac{1}{4}$ in. thick	{ 420	5	10	3.25	18.5	Rust completely removed. Dark grey surface left.	
10	Irregularly shaped piece of steel	{ 360	5	5	ca. 8.3	8.7	Rust completely removed except a little very loose rust on edges.	
11		{ ...		...	ca. 8.3	...	Not treated.	
12		{ 350	5	10	4.5	174	Rust completely removed.	
13	0.43 in. dia. $\times$ 5 in. long	{ 345	5	10	4.5	7.05		
14	Forged bar, 0.43 in. dia. $\times$ 3.4 in. long	{ 349	10	15	5.25	7.05	Most of heavy scale removed.	
15	25% chromium steel—	{ 360	10	24	6	19.4	Practically all the heavy scale removed.	
16	Mild-steel piece with weld and flame-cut edge	{ 358	5	11	5	8.9	Most of heavy scale removed.	
17		{ followed by 5	15	5.25	8.9	178	Scale removed.	
18	Sheet steel with blue scale	{ 360 375 380	6 5 10	3.5 20 20	12.3 14.5 15.7	267 117 198	Welded and flame-cut surfaces very clean.	
19								
20	Very rusty cast-iron pipe flange	{ 412	10	20	4.75-5.0	Un-certain,		
21	Rusty mild-steel sheet	{ 405	5	20	5.25	11	262	Completely cleaned. Silvery white surface.

TABLE II.—Record of Acid Pickling Experiments.

Experiment No.	Description.	Pickling Acid.		Time, Min.	Total Surface Area, Sq. in.	Remarks.
		Type.	Concentration, G. per litre.			
27	Rusty mild-steel sheet	HCl	100	37	8	Rust removed; brown stain left.
28	Rusty mild-steel sheet	HCl	100	36	8	Rust removed; brown stain left; oiled to preserve surface.
29	Rusty mild-steel sheet	H <sub>2</sub> SO <sub>4</sub>	50	71	8	Rust removed; slight brown stain left.
30	Rusty mild-steel sheet	H <sub>2</sub> SO <sub>4</sub>	50	61	8	Rust removed; slight brown stain left.
31	Steel sheet with blue scale	HCl	100	32	10	Scale not completely removed.
32	Steel sheet with blue scale	HCl	100	30	30	Scale not completely removed.
33	Steel sheet with blue scale	HCl	100	39	94	Scale not removed; deep brown stain left.
34	Steel sheet with blue scale	H <sub>2</sub> SO <sub>4</sub>	50	66	19	Scale only partly removed.
35	Steel sheet with blue scale	H <sub>2</sub> SO <sub>4</sub>	50	73	76	Scale not removed; brown stain left.
36	Sealed and rusted mild-steel sheet	HCl	100	39	10	...
37	Sealed and rusted mild-steel sheet	HCl	100	35	10	...
38	Steel sheet, one side covered with blue oxide scale, other side rusty	HCl	100	ca. 20	25	No inhibitor added.
39	Steel sheet, one side covered with blue oxide scale, other side rusty	HCl	100	ca. 20	25	0-2% Galvane added.
40	Steel sheet, one side covered with blue oxide scale, other side rusty	HCl	100	ca. 20	25	0-2% Rodine 110 added.
41	Steel sheet, one side covered with blue oxide scale, other side rusty	H <sub>2</sub> SO <sub>4</sub>	50	70	10	Best finish.
42	Steel sheet, one side covered with blue oxide scale, other side rusty	H <sub>2</sub> SO <sub>4</sub>	50	70	10	No inhibitor added.
43	Steel sheet covered with blue oxide scale and traces rust	HCl	100	ca. 20	60	0-2% Rodine 110 added.
44	Steel sheet covered with blue oxide scale and traces rust	HCl	100	ca. 20	60	0-2% Galvane added.
45	Steel sheet covered with blue oxide scale and traces rust	H <sub>2</sub> SO <sub>4</sub>	50	70	60	0-2% Rodine 110 added.
46	Steel sheet covered with blue oxide scale and traces rust	H <sub>2</sub> SO <sub>4</sub>	50	70	60	No inhibitor added.
47	Steel, thick piece containing weld and flame-cut edge.	HCl	100	ca. 20	25	0-2% Rodine 110 added.
48	Steel, irregular shape, 1 in. thick, rusted over.	HCl	100	ca. 20	25	0-2% Rodine 110 added.
49	Steel, irregular shape, 1 in. thick, rusted over.	HCl	100	ca. 20	25	0-2% Rodine 110 added.

irregular shape and not in the form of the standard test strips of which the dimensions are given in Section III, part (1).

From these experiments it was evident that ordinary rust could be removed from mild steel in a caustic bath at a temperature of 350° C. and with a current density of less than 100 amp. per sq. ft., but blue scale or temper-colours such as are produced in controlled annealing operations are not so readily removed.

On the basis of these results the conditions for the more systematic series of tests were decided on.

Also, for comparative purposes, several samples were pickled in hydrochloric or sulphuric acid under conditions which have been found to give satisfactory descaling. The results are shown in Table II.

#### (4) Scheme of Work.

A scheme was laid down for caustic-soda pickling providing all combinations of three working temperatures, 350°, 425° and 500° C. with three time periods,  $\frac{1}{2}$ , 1 and 2 min., and two values of current density, 100 and 200 amp. per sq. ft. Thus eighteen different results were obtained for each of the mild steels (steels Nos. 1-11, Table III.) and for each of the silicon steels (steels Nos. 19-24, Table IV.).

TABLE III.—*Types of Ordinary Mild Steels used in Experiments.*

Steel No.	Description.	Analysis.					Remarks.
		C. %.	Si. %.	S. %.	Mn. %.	P. %.	
1	Rusty	0.088	Trace	0.047	0.36	0.045	
2	Uniform blue scale.	0.03	0.083	0.045	0.28	0.020	Trace of nickel present.
3	Blue scaled borders.	0.062	Trace	0.049	0.20	0.027	Only outer borders of sheet used.
4	Blue scaled borders.	0.070	Trace	0.082	0.38	0.054	Only outer borders of sheet used.
5	Blue scaled borders.	0.040	Trace	0.034	0.27	0.066	Only outer borders of sheet used.
6	Blue scaled borders.	0.052	Trace	0.030	0.27	0.013	Only outer borders of sheet used.
7	Uniform blue scale.	0.068	Trace	0.021	0.31	0.025	
8	Straw temper selected.	0.059	Trace	0.049	0.22	0.018	Only temper-coloured area of sheet used.
9	Blue temper selected.	0.059	Trace	0.049	0.22	0.018	Only temper-coloured area of sheet used.
10	Killed or semi-killed	0.074	0.042	0.034	0.031	0.022	
11	Straw temper selected	0.054	Trace	0.053	0.030	0.013	Brown stain investigation only; not in comparative tests.

Owing to restricted supplies of the stainless steels, only eight tests per sample were carried out, covering the combinations of two temperatures, 425° and 500° C., with two time values, 1 and 2 min.

TABLE IV.—*Types of Stainless and Silicon Steels used in Experiments.*

Analyses of Nos. 12 to 18 made by the manufacturers.

Steel No.	Description.*	Analysis.							
		C. %.	Si. %.	S. %.	Mn. %.	P. %.	Cr. %.	Ni. %.	Ti. %.
12	S80 stainless steel.	0·11	0·43	...	...	...	16·5	1·62	...
13	Low-carbon 12-14% chromium stainless iron.	0·09	0·20	...	...	...	12·6	0·22	...
14	20% chromium stainless iron.	0·05	0·40	...	...	...	20·4	0·32	...
15	18/8 austenitic stainless steel (welding quality).	0·12	0·56	...	...	...	18·0	9·2	0·85
16	16/11 austenitic stainless steel (welding quality).	0·15	1·27	...	...	...	15·4	11·5	1·05
17	18/8 austenitic stainless steel.	0·14	0·30	...	...	...	18·8	8·6	...
18	Cutlery-type 12-14% chromium stainless steel.	0·30	...	...	...	...	12-14	...	...
19	4% silicon steel, C.A. and N.	0·024	3·96	0·016	0·09	0·032	0·08% aluminium.		
20	0·25% silicon steel, C.A. and N.	0·021	0·25	0·039	0·34	0·044	Trace aluminium.		
21	4% silicon steel, C.A.	Analyses as for corresponding close-annealed and normalised material.							
22	0·25% silicon steel, C.A.								
23	4% silicon steel, hard rolled.								
24	0·25% silicon steel, hard rolled.								

\* C.A. and N. = close-annealed and normalised. C.A. = close-annealed.

and two current values, 100 and 200 amp. per sq. ft. The stainless steels are detailed in Table IV. (steels Nos. 12-18).

The results of these experiments are shown in Table V.A. for the mild steels and in Table V.B. for the stainless and silicon types.

The main point at issue in each test is the efficacy of scale removal. Other features are the incidence of brown stain, which is discussed later, and in special cases the effects of fissures and surface flaws.

While there are anomalies in the results, due sometimes to initial differences in the scale on individual samples and to defects in the cell, a useful picture of the comparative effects of temperature, current density and time is presented.

### (5) *Modifications of the Cell.*

During the earlier series of experiments on steels Nos. 1-8 the results were occasionally disconcerting and repeat tests were made before the results could be accepted as valid. Extensive brown and even black stains developed and the cause was then obscure.

One trouble was traced to short-circuiting due to molten caustic being sprayed on to the underside of the "Sindanyo" cell cover

while electrolysis was in progress. The removal of the cover after work on Nos. 1-8 steels remedied this trouble. The grooved strips, originally of "Sindanyo," carrying the electrodes were replaced by similar fittings in steel for the same reason.

After the completion of work on all steels (except No. 11), the puzzling eccentricities of brown stain led to the elimination of the nickel anodes and copper conductor bars and the substitution of a one-piece twin welded mild-steel anode and a mild-steel cathode holder in place of the former nickel fitting. The object of this was to eliminate the possibility of electrolytic action between dissimilar metals, and it also improved the conductivity of the cell and lowered the operating voltage by about 20%. Later work demonstrated that the responsibility for brown stain could not be laid upon the non-ferrous anodes or conductor bars.

#### (6) *Efficiency of Descaling.*

Reference to Table V. shows that, in general, a slightly superior result for an equal expenditure of energy is obtained by employing the higher current density over a shorter period of time.

All the ordinary steels of Table III. may be satisfactorily stripped of scale. Steels Nos. 3-6 are moderately scaled only along the outer sides of the sheets and Nos. 8 and 9 are temper-coloured only along a central band. In all cases these oxidised areas were selected for the experiments. Prolonged treatment produces a bright silvery finish.

Ordinary heavily rusted strip is particularly easy to treat, complete stripping being obtained under all but the minimum operating conditions. The moderately thick dull-blue scales and the temper colours ranging from a straw tint to purple are more resistant, but in all cases yield to the medium or higher values of treatment.

The stainless and silicon steels are in many cases more difficult to treat than the mild steels, though, with the exception of No. 17, all may be satisfactorily stripped at the higher treatment values. Steels Nos. 14, 18 and 24 called for the maximum treatment to obtain good results, while the others yielded to the lower or medium values.

#### (7) *Removal of Sponge Iron after Descaling.*

The black film of sponge iron which remains on the surface of the sheet after treatment is easily removed on quenching in cold water. Much of it is immediately dispersed in the water and a light brushing afterwards quickly removes the remainder. An immersion in boiling water completes the operation.

In certain cases, such as sheet heavily rusted on one side or the steels of the types of Nos. 4, 5 and 6, one side is often found to be considerably rougher than the other, and very vigorous brushing is required to remove the sponge iron embedded in the pitted surface.

**TABLE V.—Results of Descaling Experiments : (A) Mild Steels, (B) Stainless and Silicon Steels.**

Except for Nos. 13, 15 and 16, for which sufficient metal for 8 specimens only was available, 18 test-pieces were prepared from each material. The specimens were numbered from 1 to 18, and the individual results are entered in the Table in accordance with the "key to specimen numbers" at the foot.

Steel No.	Description.		Time, Min.	Current Density and Temperature.			
	Untreated Surface Finish.	Appearance after Treatment.		100 amp. per sq. ft. at—	200 amp. per sq. ft. at—	350° C.	425° C.
1	Rusty sheet.	A.—Mild Steels.	1/2	X	x	4	4
2	Smooth blue scale, moderately thick.		1/2	4	4	4	4
3	Dull blue scale, moderately thick.	s probably due to short-circuit.	1/2	X	X	4	4
4	Dull blue scale, moderately thick.		1/2	X	X	4	4
5	Dull blue scale, moderately thick.		1/2	X	X	4	4
6	Dull blue scale, moderately thick.	Stain mainly on rough side.	1/2	X	X	4	4
7	Smooth blue scale, moderately thick.	Slight stain only, except specimen 18.	1/2	X	X	4	4
8	Smooth straw/blue temper colour.	Specimens 10-12 difficult to distinguish stain. Specimen 17 slight stain only.	1/2	X	X	4	4
9	Smooth blue temper colour.	Specimen 16 slight stain only.	1/2	X	X	4	4
10	Killed steel. Thick blue scale, streaked. Streaks remained visible after descaling.		1/2	X	X	4	4

												Key to Specimen Numbers.																			
												1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
12	SS0 stainless steel. Smooth blue, moderately thick scale.																														
13	Low-carbon, 12-14% chromium stainless iron. Smooth purple, moderately thick scale.																														
14	20% chromium stainless iron. Smooth blue, moderately thick scale.											All except specimens 1 and 2 nearly completely descaled. Specimen 18 very bright.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
15	18/8 austenitic stainless steel (welding quality).											Specimen 17 slight stain only.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
16	16/11 austenitic stainless steel (welding quality). Dull blue and rusty scale.											Specimen 17 slight stain only.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
17	18/8 austenitic stainless steel. Patchy scale and rust spots.											Specimen 17 nearly completely descaled.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
18	Cutlery-type 12-14% chromium stainless steel. Thick scale and rust.											Specimen 17 nearly completely descaled.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
19	4% silicon steel, close-annealed and normalised. Thick scale both sides.											Specimen 6 stain due to contact. Specimens 8, 9, 17 and 18 very slight stains.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
20	0.25% silicon steel, close-annealed and normalised. Moderately thick scale both sides.											Specimen 9 stain by rough surface. Specimen 13 stain due to contact.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
21	4% silicon steel, close-annealed. Thick scale one side; patchy on reverse.											Specimens 17 and 18 stains due to contact.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
22	0.25% silicon steel, close-annealed. Thick patchy scale one side; very little scale on reverse.											Specimens 17 and 18 stains due to contact.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
23	4% silicon steel, hard rolled. Thick scale one side; practically none on reverse.											Stain only slight in all cases.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
24	0.25% silicon steel, hard rolled. Moderately thick scale both sides.											Specimen 6 very good silvery surface one side. Specimen 9 very slight stain only. Specimens 14, 15 and 17 stains due to contact.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	

## KEY TO RESULTS.

4. Satisfactory descaling without brown stain.
2. Satisfactory descaling on one side only; without brown stain.
- X. Unsatisfactory descaling on both sides.
- z. Unreliable results; probably short-circuit.
- S. Large areas brown stain, otherwise satisfactory.
- s. Small areas brown stain, otherwise satisfactory.

(8) *Drying-off after Brushing.*

This operation should be expedited in every way possible, such as by hot-air currents. Delay in the removal of the last traces of water frequently gives rise to staining.

(9) *Investigation of Causes of Brown Stain.*

This defect in the work has been more or less in evidence throughout the series of experiments.

A statistical examination of the results was carried out in order to discover whether any of the factors, time, temperature or current density, might be associated with its occurrence. Fifteen types of sheet, excluding the stainless steels, were considered. The results as shown in Table V. were variously arranged into groups of particular time, temperature or current characteristics. Graphs were thus obtained showing the trend of the frequency with which brown stain was observed under separately changing conditions of time, temperature and current.

From this analysis, temperature emerged as the major causative factor in producing brown stain. Above 400° C. there are increasing tendencies towards its appearance.

At this stage of the experiments, the stain was suspected to be associated with the use of the nickel electrodes, and further work was undertaken to establish this point.

As mentioned above, an all-steel electrode fitting was made for the cell and experiments with the straw-temper-coloured strip, previously found to be susceptible, were continued. Brown stain still occurred, but on a greatly reduced scale. The nickel anodes with copper conductors, alone and together with the nickel cathode holder, were reintroduced, but the frequency of brown stain remained at an insignificant level.

Straw temper-coloured sheet (No. 11), similar to the sample used in the series (No. 8), was tested with other types previously used under the original conditions of the cell. The brown stain still appeared infrequently and its source remained obscure.

It was observed that the stain might appear indiscriminately under any conditions of moderate or excessive treatments with regard to either time or current density. While it appeared fortuitously, it invariably disappeared after a few seconds' further treatment in the cell. Very occasionally the original stain would vanish, only to be replaced by another of quite different form. The impression was formed that the stain had its origin in the local conditions surrounding the work previous to or during its removal from the cell, and the investigation proceeded along this course.

Brown stains thus identified conveniently fall into the following classes :

*Type A.*—This brown stain (Fig. 7(b)) has been frequently noticed in work upon ordinary rusty mild-steel sheet temper-

coloured, and the silicon types, and is more prevalent at the 500° C. temperature.

It is known that the solubility of  $\text{Fe}_2\text{O}_3$  in molten NaOH rises steeply with increased temperature. It has been shown \* that at 350°, 400° and 500° C. the solubility per 100 g. of NaOH is, respectively, 0.0011, 0.0057 and 0.06 g. of  $\text{Fe}_2\text{O}_3$ , and that on cooling the phase  $\text{NaFeO}_2$ , sodium ferrite, separates.

$\text{NaFeO}_2$  is also produced by the dissolution of finely divided iron in molten NaOH. The dissociation or hydrolysis of sodium ferrite is suggested as the fundamental cause of brown stain. Tainton also expresses the view that brown stain is consequent on the formation of sodium ferrite.<sup>(5)</sup>

On removing the work from the cell, there is a film of NaOH rich in dissolved (and perhaps suspended)  $\text{NaFeO}_2$ . Yellow-brown crystals of this may be observed to separate as the work cools. The iron-laden film drains and often forms a comparatively thick layer along the edges or bottom of the work. If quenching is carried out while the film is still molten, a bronzed stain develops at the site of the thickened film. If, however, the caustic film first solidifies before quenching, the stain is greatly reduced, but the work, in general, suffers in the brilliance of the finish.

A variant of this type of stain is shown in Fig. 7(a), in which small circles of stain surround minute pits in the metal surface.

*Type B.*—A more diffused brown stain occurring in patches results from a delay of from  $\frac{1}{2}$  to 2 min. in the removal of work from the cell after switching off the current, and the statistical examination showed that this "delayed-removal" type is more prevalent at the 500° C. temperature.

It is believed that this type mainly accounts for the apparently higher incidence of brown stain in the early stages of these experiments, and, as handling technique improved, the stains from this source diminished. The formation of this type under large-scale conditions of uninterrupted current seems improbable. This type when developed at high temperature is visible on the work before quenching and remains fixed under all conditions of quenching (*cf.* type *A* stains).

*Type C.*—If, when current has been passing for a period, the work is shorted over to the anode either before or after switching off, a heavy current discharge takes place and severe and extensive dark-brown or black stain develops.

*Type D.*—When a cell has been in operation for some days, the electrolyte becomes heavily contaminated with sodium ferrite,<sup>(6)</sup> and very occasionally aggregates of discoloured crystals lodge on the freshly removed work. On

\* W. S. Macfarlane, private communication.

quenching, especially while the work is hot, brown stain will invariably appear at such places.

*Type E.*—Some brown stain is always found at the point of contact between the work and the holder, irrespective of whether the latter is steel or nickel.

*Type F.*—Another source of brown stain in characteristic ripple form is the interrupted quenching of hot work (see Fig. 7(c)). It occurs at the water-lines where interruption occurs. This is a minor form of stain, and cannot be regarded as a serious blemish.

*Type G.*—This is not a true brown stain. It is observed when work has received insufficient treatment with regard to time and/or current, and probably consists of residual scale or rust.

It will be seen that brown stain arises under varying circumstances, and may usually be classified under one of the heads *A* to *G* described above.

Type *A* is, as may be expected, more liable to arise at high temperatures, and is minimised by draining off adherent electrolyte before quenching. The use of the air blast in full-scale practice would probably eliminate it.

Type *B* is obviated by maintaining the current up to the instant of removing the work from the cell, and is therefore unlikely to occur in a continuously operated plant.

Type *C*, closely related to the preceding, can arise only through a breakdown in the insulation of the electrode poles.

Type *D* is likely to occur where the electrolyte is old and sludge-contaminated.

Type *E* may not arise in large-scale practice where there is no fixed connection between the work and the electrodes.

Type *F* points to the desirability of prompt and steady quenching of the entire work without interruption.

Type *G* requires no comment.

It is further established that copper conducting bars with nickel cathode holders, and excessive currents and times are not material factors in the production of brown stain, but that control of temperature, maintenance of a clean electrolyte, good insulation, expeditious removal of the work from the cell and proper control of the quenching are the important factors in preventing stain.

#### (10) Removal of Brown Stain.

Brown stain of all types is indelible and cannot be removed by brushing or scouring.

A further brief treatment lasting only a few seconds in the molten caustic cell provides a certain means of eliminating all types of brown stain. Tainton<sup>(5)</sup> suggests keeping the exit end of the caustic bath at a low temperature, withdrawing the articles into

an inert gas in which they are allowed to cool down, agitation in the fused salt before removal, or reduction of the current density to a low figure before removal.

Apart from the disfigurement, no information is at present available regarding any detrimental influence of brown stain on subsequent operations such as galvanising.

The occurrence of brown stain has been dealt with in some detail, but the author does not wish to imply that it is a serious defect of the caustic pickling process. On the contrary, once the design of the experimental cell had been modified to provide the best possible electrical connections, and also when the operator became sufficiently skilled to carry out the various stages of the process with a minimum of delay, it became a matter of some difficulty to produce brown stain. It is felt that in a full-scale continuous plant the trouble is unlikely to be experienced to any appreciable extent.

#### (11) *Photographic Records of Experiments.*

In the course of the investigation, photographic records were made of all the experiments set out in Table V. It is not possible to publish all these illustrations, but some representative examples are shown in Figs. 8 to 13.

Areas incompletely descaled appear black or nearly black; brown stains appear a lighter shade, while the descaled areas are white or pale grey.

In many cases the front and back surfaces of the sheets differed considerably in thickness of scale and the character of the surface below the scale. This sometimes resulted in differences of behaviour in the pickling operation. Where such differences occurred they are indicated by cutting the specimen into two and exhibiting half of the front and half of the back surface (*see also* paragraph 13 below).

#### (12) *Summary of Results.*

The experiments carried out show clearly that the results of the treatment are better as the time, temperature and current density are increased. It is recommended that 425° C. and 200 amp. per sq. ft. should be regarded as minimum conditions, and that the time should be adjusted according to the type of scale to be removed. It will probably be of the order of 1 min., except in the case of certain highly alloyed steels, such as stainless, which may require a higher current density or a time as long as 4 min.

In the descaling of wire, much higher current densities than 200 amp. per sq. ft. are used. Experience may show that such conditions are advantageous for other applications.

#### (13) *The Effect of Surface Finish.*

It was observed in the course of the experiments that variations in the surface of sheet steel affected the ease or otherwise with

which scale could be removed. For example, steel sheets are often rolled in pairs, and the outer surfaces which make contact with the rolls are usually smoother than the two inner surfaces which have been in contact with each other. In cases where the difference between the two sides of a specimen caused a difference in the removal of scale by caustic pickling, this has been indicated by halving the specimen and reversing one half when arranging the specimens for photographing. The following conclusions may be drawn from the observations made :

- (a) The surface most readily descaled is a smooth matt surface normally found beneath an oxide layer of medium thickness.
- (b) A polished surface covered with a very thin layer of oxide in the form of a straw or blue temper-colour is less easily descaled.
- (c) A thick scale is usually easy to remove, unless the underlying surface is pitted and irregular for some reason, such as having had scale rolled into it.
- (d) The sample of killed steel (No. 10) which was examined had on its surface numerous streaks, about  $\frac{1}{32}$ – $\frac{3}{16}$  in. wide, running in the direction of rolling. These marks remained after descaling. The streaks were not related to the micro- or macro-structure of the steel, which was that of a normalised mild steel.

#### (14) *The Hydrogen Content of Pickled Mild Steel.*

Hydrogen was determined in several samples of a mild-steel sheet. The results are as follows :

	Hydrogen Content, Ml. per 100 g.
Original sheet—scale cleaned off with emery cloth.	(1)      3.70
	(2)      3.65
Descaled in caustic soda—tested 2 days after treating.	(1)      3.03
	(2)      3.26
Descaled in caustic soda—tested 9 days after treating.	(1)      3.39
Acid pickled (HCl with inhibitor)—tested 2 days after treating.	(1)      4.21
	(2)      4.06
Acid pickled (HCl with inhibitor)—tested 9 days after treating.	(1)      4.29

These results indicate that no hydrogen was absorbed during the caustic pickling. On the contrary, some hydrogen was driven off, probably as a result of the temperature to which the steel was heated (500° C.). Acid pickling resulted in a slight increase in the hydrogen content.

The hydrogen determinations were made by the vacuum heating method.<sup>(7)</sup>

#### (15) *Attack on Metals by Electrolytic Pickling.*

Metal which is treated by electrolytic pickling in molten caustic soda is exposed to the conditions of the process for such a short

period that loss of weight is infinitesimal and may normally be entirely disregarded. The author, however, had several instances brought to his notice of attack on various parts of the plant used in full-scale working, and this led to investigations which have thrown considerable light on the subject. The parts affected are the mild-steel tanks which hold the molten caustic soda, and the nickel anodes and their mild-steel shields.

As regards the tanks, cases of the perforation of mild-steel plates 1 in. thick have been examined. The defect is invariably immediately behind the anodes, and deterioration appears to take place more rapidly as the distance between the anodes and the tank wall decreases. For example, a tank became perforated after a fairly long period of service, and it was repaired by welding a plate on the inside of the tank, covering the perforation. This plate failed after a comparatively short period and most rapidly at a point where it had buckled, still further reducing its distance from the anodes.

The anodes consist of strips of nickel 4 in. wide by  $\frac{1}{2}$  in. thick, and they dissolve slowly. After long service evidence of thinning is observed near the bottom. The anode shields are made of  $\frac{3}{16}$ -in. mild steel and they cover the anodes except on a part of one side facing the cathodes. They are insulated from the anodes, but, as will be explained later, the whole question of insulation presents great problems in baths of molten caustic soda. The anode shields failed rapidly (14–21 days).

The experimental electrolytic cell (Fig. 1) was rigged up for the determination of the loss of weight of both anodes and cathodes, and several tests were made, with the results given in Table VI.

TABLE VI.—*Loss of Weight of Electrodes.*

Total Time. Hr.	Quantitative Electrode.	Amp. per sq. ft. through Quantitative Electrode.	Mean Temp. ° C.	Mean Volts.	Loss from Quantitative Electrode, G. per sq. ft. per hr.	Notes.
4 $\frac{1}{2}$	Mild-steel cathode.	330	385	2.6	11.20*	Twin mild-steel anodes used.
4 $\frac{1}{2}$	Mild-steel anode.	330	375	2.6	2.49	Twin anodes used as cathode.
4 $\frac{1}{2}$	U-shaped mild-steel cathode.	165	385	2.65	2.54 *	Perforated mild-steel anode placed above and within area of U-shaped cathode.
16	Mild-steel sheet.	Nil	380	Nil	0.0074 grain	

\* These figures correspond roughly with a rate of attack proportional to the square of the cathode current density.

These experiments demonstrate beyond question that both anodes and cathodes are attacked by the electrolytic process.

A careful examination of a full-scale plant engaged in cleaning

steel wire showed that considerable current leakages were taking place. The evolution of gas from the anodes and cathodes causes caustic soda to be sprayed on the under side of the lid covering the caustic-soda tanks, bridging various components which are intended to be insulated from one another and/or attacking the insulators. The following voltage measurements on three units of the plant illustrate this:

	Unit No.:	2.	3.	4.	
At electrode . . . .	4.35 volts.	4.3	volts.	4.4	volts.
Anode to anode shield . . . .	1.44 "	1.4	"	1.4	"
Anode shield to lid . . . .	0.8 "	0.62	"	1.8	"
Anode to lid . . . .	2.3 "	2.0	"	3.0	"
Lid to cathode . . . .	2.4 "	2.4	"	1.5	"
Tank to lid . . . .	0.32 "	0.1	"	0.4	"
Anode to tank . . . .	1.8 "	2.0	"	3.0	"
Tank to cathode . . . .	3.0 "	2.4	"	1.5	"
Tank to heater tube . . . .	0.22 "	0.11	"	0.03	"
Heater tube to lid . . . .	0.10 "	0.02	"	0.55	"
Cathode support to cathode . . . .	2.0 "	2.0	"	1.7	"
Cathode support to lid . . . .	0.4 "	0.3	"	0.5	"
Heater tube to earth . . . .	...	...	...	3.6	"
Tank to tank : Unit 4 to unit 2 . . . .		8	volts.		
" 4 " 3 . . . .		3.6	"		
" 3 " 2 . . . .		4.3	"		

A further laboratory experiment was carried out to examine the probability of attack on the wall of the cell when the latter is in close proximity to the anode. Electrodes, consisting of an anode of nickel sheet bolted to a nickel holder, and a cast-iron cathode were placed in the experimental cell about 4 in. from each other. Interposed between each electrode and the end wall of the cell was a weighed mild-steel strip, firmly clamped to the upper rim of the cell itself. These strips could be regarded as internal projections of the cell brought nearer to the active electrodes. The weighed strips were at an equal distance ( $\frac{3}{4}$  in.) from the electrodes and the cell walls. A current of 20 amp., equivalent to 200 amp. per sq. ft. of electrode area, was passed for 18 hr. with the electrolyte (caustic soda) at a temperature of 395–415° C. The voltage remained steady at 2.75–2.78 V. The weighed strips were then disconnected, washed and again weighed.

The strip which had been near the anode lost 0.0292 g.; it appeared to be heavily etched on its upper portion, while the lower portion was covered with oxide.

The strip which had been near the cathode had gained 0.0330 g. and was completely covered with oxide, which was thicker near the top (see Fig. 2).

The weighed strips were then refitted in the cell and the current was applied for a further 22 hr. under similar conditions. This time there was a similarly graduated attack and oxidation; the

strip near the anode lost 0·0270 g., and the one near the cathode gained 0·0612 g.

An examination of the foregoing data, together with the experience of full-scale plant operation, suggests that the distance of the anodes from the tank walls and the relative positions of anodes and cathodes are of primary importance. The current will choose the easiest path, and it is suggested that in place of the usual arrangement in which the anodes hang down the sides of the bath with the U-shaped cathodes between them (Fig. 3(a)) the anodes might be placed within the U-shaped cathodes (Fig. 3(b)). This ensures that the easiest path

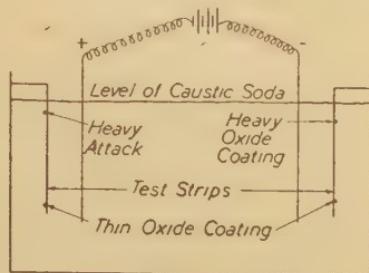


FIG. 2.—Diagram of the Cell to Demonstrate Attack on the Cell Walls.

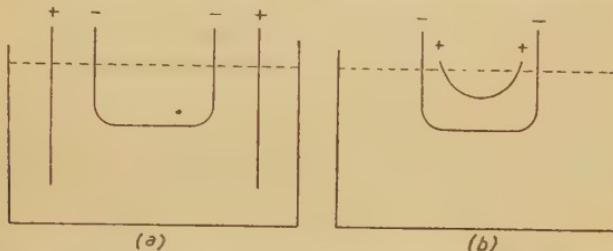


FIG. 3.—(a) Conventional Arrangement of Anodes and Cathodes. (b) Suggested Arrangement of Anodes and Cathodes to Eliminate Attack on the Cell Walls.

for the current is the direct one between the anodes and cathodes, and the anodes are as far as possible from the walls of the tank. This arrangement should improve the electrical efficiency of the plant. It might be found desirable to construct the anodes of perforated sheet or bend them longitudinally to a U-shape, to facilitate the escape of the evolved gases.

#### IV.—THE DESIGN OF PLANT FOR CARRYING OUT THE PROCESS.

It is not intended to give here the detailed design of plant for carrying out the caustic pickling process, but merely to describe the general outline and indicate a few of the points which should be considered in order to give efficient and safe working.

##### (1) Construction of Tanks.

Tanks for containing molten caustic soda should be constructed of mild-steel plate about 1 in. thick, and with the joints welded. Electric welding is recommended and the joints should be welded

from both sides. Another method which has given several years' satisfactory service is to use flanged and riveted joints, caulked on the inside by welding.

#### (2) *Method of Heating the Caustic Soda.*

Immersed gas-heated tubes have been used with some success. Another method is to build the caustic-soda tank into an outer tank containing molten lead. The author is of the opinion that methods which involve heating the tank from the outside are not so desirable as internal methods. Gas flames playing on the outside are apt to cause scaling and local overheating, leading to deterioration of the tank itself. Sludge which collects on the bottom of the tank interferes with heat transfer. Submerged gas-heated tubes are satisfactory, provided that they are kept clear of the sludge layer, but the most satisfactory method is probably to use electric immersion heaters which are suspended along the sides of the tank and can be readily taken out for inspection or replacement. Such heaters are known to have a long life in molten salts at temperatures up to 530° C., and, provided that they are kept well away from the anodes, they would be expected to last satisfactorily even under conditions where electrolysis is taking place.

#### (3) *Collection and Removal of Sludge.*

The amount of sludge formed by electrolytic pickling is considerable, and the molten caustic tank should be made at least 12 in. deeper than the working depth, so that the layer of sludge is well below the heaters, electrodes and work.

Provision must be made for the regular removal of sludge at intervals of ten days or so. The most satisfactory method is to cover the bottom of the tank with removable trays 4-6 in. deep and with  $\frac{1}{4}$ -in. perforations in the sides. It should be possible to lift the lid of the tank with the electrodes, &c., as one unit, so that the sludge trays could then be lifted out of the molten caustic soda, allowed to drain, emptied and replaced without a prolonged stoppage of the plant.

#### (4) *Removal of Sponge Iron from the Work.*

Sponge iron is present on the treated work as a very fine layer which can normally be easily removed. The method to be adopted for its removal will depend on the type of metal being treated, e.g., wire, sheet or fabricated parts. Tainton recommends quenching in cold water, washing, brushing, or making the treated material the anode in an aqueous solution of either caustic soda or sulphuric acid. Scrubbing by means of revolving steel wire-brushes would probably remove the deposit satisfactorily from sheet metal. It is important to avoid passing the treated metal between rollers, as this has the effect of consolidating the sponge-iron layer and making it adhere strongly to the parent metal.

(5) *Insulation and Protection.*

In order to avoid unnecessary loss of heat, the tank and lid should be well lagged with brickwork. The lid should always be closed while the process is operating, not only to conserve heat but also to trap the caustic-soda spray. Plants should be designed for automatic operation, but when it is necessary for workmen to carry out adjustments, charge fresh caustic soda or remove sludge trays, they should be protected by comfortable goggles, rubber boots, rubber or cotton gloves or aprons, and cotton protectors for the face and head. Facilities should be available for the immediate treatment of caustic burns by flushing with liberal quantities of 5% aqueous ammonium chloride solution. The importance of this, particularly when caustic soda gets in the eye, cannot be overstressed. Insistence on the use of protective clothing, however, is the surest safeguard against injury.

(6) *Bearings for Use in Molten Caustic Soda.*

When bearings have to function in molten caustic soda, as in the mechanism for propelling sheet steel through the bath, they should be made of cast iron.

(7) *Electrical Contacts.*

The maintenance of good electrical contacts appears to be an important factor in preventing the occurrence of brown stain on treated material.

(8) *Power Requirements.*

These are stated<sup>(1)</sup> to be 5–20 kWh. per ton of metal cleaned and 1 gal. of fuel oil or its equivalent per ton of steel heated.

## V.—NOTE REGARDING ABSENCE OF EXPLOSION RISKS.

There is no risk of explosions occurring through oxygen and hydrogen evolving from the electrodes and mixing at atmospheric

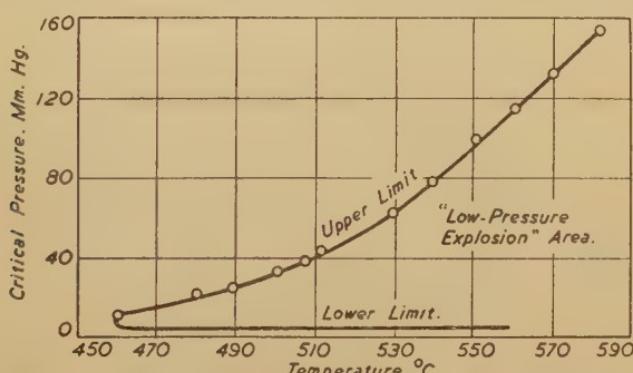


FIG. 4.—Low-Pressure Explosion Area for Mixtures of Oxygen and Hydrogen.

pressure beneath the lid of the electrolytic pickling plant. The "low-pressure explosion area" <sup>(8)</sup> is shown in Fig. 4, from which it is evident that a temperature very much higher than 500° C. must be reached before an explosion could occur at atmospheric pressure.

#### ACKNOWLEDGMENTS.

The author acknowledges assistance received from a number of his colleagues, namely, Dr. C. W. Bunn, who prepared the X-ray photographs (Fig. 6), Mr. S. W. Craven, who carried out the hydrogen determinations, Mr. R. Threlfall, who supervised the electrical tests, and Mr. L. H. Tomlins, who carried out most of the other practical work involved in the investigation.

Valuable help has also been given by Messrs. J. Sankey & Sons, Ltd., who are experimenting on the descaling of sheet steel, in agreement with the patentee, Mr. U. C. Tainton, by Messrs. Rylands Bros., Ltd., who are operating the process, and by Messrs. Brown Bayley's Steel Works, Ltd., who kindly provided the samples of stainless steel.

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#### CORRESPONDENCE.

Mr. C. D. S. BRIDGETT (Messrs. J. V. Rushton (London), Ltd., London) wrote : This process would appear to be suitable only for wire, strip and bar materials, since the temperatures used—anywhere between 350-500° C.—preclude the possibility of using it on fabricated articles, owing to the liability of distortion by heat.

In Section V. the author states there is no risk of explosion through oxygen and hydrogen evolved from the electrodes. There may not be from this cause, but has the author ever seen a damp article placed in a bath of molten caustic soda ? If so, he will realise that this is a highly dangerous material to use unless one can

guarantee that the articles to be immersed are going to be dry; this was evident in the old "black oxide" process for corrosion prevention on steel.

If the writer's memory is correct, one of the claims in the original patent was that the oxide was reduced, by sodium produced at the cathode, to pure iron, and left a very smooth surface suitable for zinc-plating; but on p. 296 P the author refers to the removal of the sponge iron formed, and this would not appear to agree with the original patent.

Dr. T. P. HOAR (Metallurgical Laboratories, Cambridge) wrote : I am interested in the actual electrode reactions that take place in cells with molten electrolytes, and I should appreciate any further information that the author can give with regard to such matters as the amount of hydrogen evolved at the cathode, and the current efficiency of the reduction of the scale to iron, if indeed it is possible to compute this. I take it that there is no direct experimental evidence of the production of metallic sodium at the cathode, at any rate until the descaling process is complete; and if this is indeed the case, I think it is unnecessary and even incorrect to postulate its production as an intermediate stage at the cathode. May we not visualise the cathodic process of oxide reduction merely as the emergence of oxide ions from the oxide lattice into the electrolyte and their replacement by electrons?

Dr. J. C. HUDSON (Birmingham) wrote : It would add to the value of the data for the hydrogen content of pickled mild steel given in section (14) of the paper if Mr. Evans would add details of the conditions of the acid pickling used, *i.e.*, concentration of hydrochloric acid, temperature and duration of pickling, nature of the inhibitor, &c., since these might affect the value obtained. Further, if possible the metallurgical history of the original sheet should be stated, *e.g.*, whether it had been pickled at an intermediate stage at the works or not, since this would also have a bearing on the results.

The view has been advanced in certain quarters that blistering of a paint film applied to a pickled steel surface might be caused by the gradual evolution from the metal of hydrogen absorbed during the pickling process. I doubt this, but to settle the matter data such as those given by the author are required; indeed, it might prove profitable to make a special study of the effect of different pickling methods on the hydrogen content of pickled steel.

#### AUTHOR'S REPLY.

Mr. N. L. EVANS wrote in reply : So far as I am aware, the electrolytic pickling process in molten caustic soda has only been

used commercially for descaling wire and strip, but the temperature involved would not appear to preclude its use for fabricated articles, in view of the fact that much higher temperatures are used in other finishing processes, notably vitreous enamelling, without harmful distortion taking place.

Mr. Bridgett is right in drawing attention to the danger involved if damp articles are introduced into a bath of molten caustic soda. It is not, however, difficult to ensure that material which is to be treated is perfectly dry; and in the paper stress is laid on the desirability of designing the plant for automatic operation, so that the risk of accident is minimised by keeping personnel in protected positions. The manufacturers of alkali are always ready to place their experience in such matters at the disposal of users. The speed of descaling by this process gives it such marked economic advantages over other methods of descaling that it is well worth while going to considerable trouble to design suitable plant, incorporating well-tried safety devices.

The iron produced by reduction of the oxide scale needs to be removed from the surface of the treated material before any subsequent operation such as galvanising can be carried out. The reduced iron is present in a very loosely adhering condition, either as a fine powder or as a thin foil, such as is illustrated in Fig. 5. A light brushing or wiping operation or an anodic treatment is sufficient to remove it.

Regarding the points raised by Dr. Hoar, the investigation was concerned solely with the practical application of the process and no measurements, such as the amount of hydrogen evolved at the cathode, were made.

No direct experimental evidence of the production of metallic sodium at the cathode was obtained in the course of the present investigation, but, as the electrolysis of molten caustic soda is the standard method of producing metallic sodium, it seemed justifiable to assume this as a working hypothesis.

Since the paper was published, there have been important developments, and a much simpler, non-electrolytic process is now under investigation. The reducing agent in this case is sodium hydride dissolved in caustic soda. It is hoped that this may form the subject of a further communication.

In reply to Dr. Hudson's enquiry, the conditions of the acid pickling experiments in section (14) of the paper were :

100 g. per litre of hydrochloric acid, plus 0·2% of Galvene,  
used at room temperature.

The duration was unfortunately not recorded, but was probably about 20 min. The previous history of the sheet is not known, but the results in section (14) are comparable with one another, as all the samples were cut from the same sheet of metal.

# THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN PIG IRON.<sup>1</sup>

BY THE BLAST-FURNACE MATERIALS ANALYSIS SUB-COMMITTEE OF THE BLAST-FURNACE COMMITTEE.<sup>2</sup>

## SUMMARY.

An account is given of the work of the Sub-Committee on the determination of sulphur and phosphorus in pig iron, and details are put forward of methods recommended for accurate work.

Suggestions are made as to the most appropriate methods of sampling iron, whether in the form of pigs or in the molten state.

The combustion method for sulphur determination is described in detail and the work of members of the Sub-Committee in the development and standardisation of the method is set out.

The work reported on the estimation of phosphorus in pig iron includes a study of the possible effects of arsenic and titanium on the results.

## INTRODUCTION.

At a meeting of the Blast-Furnace Committee held on June 23rd, 1938, consideration was given to the variations in analysis, particularly with respect to sulphur content, believed to occur during the progress of a cast from the blast-furnace. It was apparent from the outset that an investigation of this subject would require a sound background of analytical and sampling technique, and a Pig Iron Analysis Sub-Committee was appointed to carry out the necessary preliminary investigation. Subsequently the terms of reference of the Sub-Committee were extended to cover the investigation of analytical methods for all constituents of pig iron and for ores, &c.

The present constitution of the Sub-Committee, renamed the Blast-Furnace Materials Analysis Sub-Committee, is as follows :

Mr. J. B. Fortune ( <i>Chairman</i> )	Millom and Askam Hematite Iron Co., Ltd.
Mr. R. S. Crowle	Millom and Askam Hematite Iron Co., Ltd.
Dr. E. Gregory	The Park Gate Iron and Steel Co., Ltd.
Professor H. F. Harwood	Formerly of the Imperial College of Science and Technology.
Mr. R. McGregor	The Appleby-Frodingham Steel Co., Ltd.
Mr. A. Murray	Messrs. Colvilles, Ltd.
Mr. H. R. Pepper	Messrs. Stewarts and Lloyds, Ltd. (Corby).
Mr. E. Taylor-Austin	The Darwen and Mostyn Iron Co., Ltd.
Mr. R. C. Tucker	Messrs. Newton Chambers & Co., Ltd.

<sup>1</sup> Received July 22, 1943.

<sup>2</sup> A Committee of the Iron and Steel Industrial Research Council.

Mr. W. Westwood \* . . . The British Cast Iron Research Association.

Mr. J. H. Wright \* . . . Messrs. Dorman Long & Co., Ltd.

Mr. J. M. Ridgion (*Secretary*) The British Iron and Steel Federation.

\* Mr. Westwood and Mr. Wright joined the Sub-Committee after the work on the determination of sulphur was complete.

The Sub-Committee have carried out a survey of methods in current use for the determination of silicon, manganese, phosphorus and sulphur in pig iron, and have examined a number of alternative techniques for sampling. The results of this work led the Sub-Committee to make a detailed study of methods for the determination of sulphur and phosphorus, resulting in the setting up of standardised methods for the estimation of these elements as described below.

### SAMPLING.

The Sub-Committee recommend the following alternative methods, depending on whether the iron is in the form of pigs or in the molten state.

#### *Pig Sampling.*

The sample shall be taken by drilling vertically through the cross-section of the pig as in Fig. 1, a  $\frac{3}{4}$ -in. dia. flat drill being used.

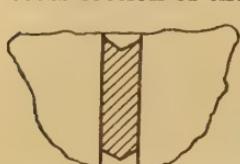


FIG. 1.—Method of Sampling the Pig.

The surface of the pig having been scratch-brushed, the top skin shall be penetrated and these drillings discarded. The sample shall then be taken by drilling almost through the pig, care being taken, however, not to penetrate the bottom skin. The greatest precautions shall be taken to avoid contamination of the sample by sand detached from the surface of the pig. The separation of the sample by means of a magnet should be avoided when possible, however.

#### *Molten Samples.*

Samples from a stream of iron shall be taken by the pot sampling method: The samples may be approximately 2 in. cube, or cylindrical of diameter  $1\frac{1}{2}$ –2 in. and length approximately 2 in. (Examples of suitable sampling pots are shown in Figs. 2 and 3.) They shall be drilled according to the method described for pigs. No difficulties due to adhering sand will be experienced in this case.

If the iron is too hard to be drilled, a shallow mould ( $\frac{3}{8}$  in. deep) should be used and the sample quenched in water from a black heat. After breaking into small pieces the sample may be crushed to pass a 100-mesh sieve.

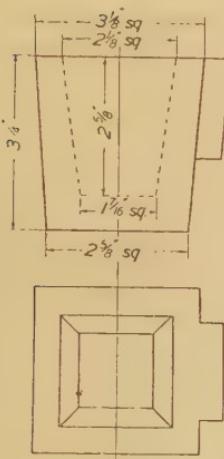


FIG. 2.—Square Sampling Pot.

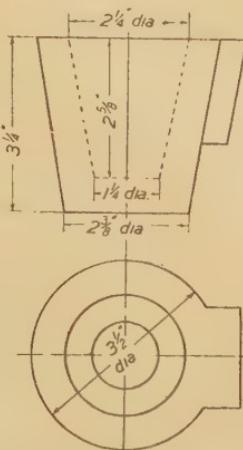


FIG. 3.—Circular Sampling Pot.

### THE DETERMINATION OF SULPHUR IN PIG IRON.

The preliminary exchange of samples for analysis by members of the Sub-Committee, using normal routine gravimetric, volumetric and combustion methods, was carried out. It is not proposed to set out the various results in detail, as the divergences reported were very considerable, owing to the variety of methods employed. As a result of this work, the Sub-Committee agreed to focus their attention on the improvement of the combustion technique as the most promising method. A series of analyses in which special precautions were taken to standardise the  $N/200$  sodium hydroxide solution suggested that the method was truly stoichiometric, but the difficulties of standardising and maintaining the solutions required were such that the Sub-Committee preferred to base the recommended method on comparison with a steel sample of known sulphur content. In this connection it was appreciated that the gravimetric method possesses advantages over a secondary method based on a known standard, but it was felt that, particularly in the case of hematite irons of low sulphur content, the difficulties of controlling the gravimetric method were too great.

The results in Table I. are given as an example of the correspondence which can be attained between different laboratories using the standardised combustion method.

#### *Description of the Method.*

The principle of the method consists in burning the sample in a rapid stream of oxygen at a temperature of  $1250-1300^{\circ}\text{C}$ . During the ignition the sulphur is evolved as  $\text{SO}_2$ , which is absorbed in

TABLE I.—*Sulphur Determinations in Pig Irons by the Standardised Combustion Method. Comparison of Results obtained in Different Laboratories.*

Analyst.	Sulphur, %, in—		
	Sample A.	Sample B.	Sample C.
I. . . . .	0·0437	0·123	0·0084
II. . . . .	0·0347	0·1238	0·0055
III. . . . .	0·0418	0·1242	0·0061
IV. . . . .	0·037	0·127	0·0056
V. . . . .	0·0424	0·1238	0·0123
VI. . . . .	0·0367	0·1254	0·0053
VII. . . . .	0·041	0·1238	0·0074
VIII. . . . .	0·040	0·124	0·0070
IX. . . . .	0·0344	0·1217	0·0064
Mean . . . . .	0·0391	0·1241	0·0071
High-Mean . . . . .	0·0046	0·0029	0·0052
Mean-Low . . . . .	0·0047	0·0024	0·0018
Mean error * . . . . .	0·0035	0·0015	0·0022

\* Mean error =  $\sqrt{\frac{\sum \delta^2}{n-1}}$ , where  $\sum \delta^2$  = sum of squares of deviations from the mean for the  $n$  results.

neutral silver nitrate solution. The nitric acid set free is titrated with sodium hydroxide solution, methyl red being used as indicator.

The apparatus used is shown in diagrammatic form in Fig. 4, details of the constituent parts being given.

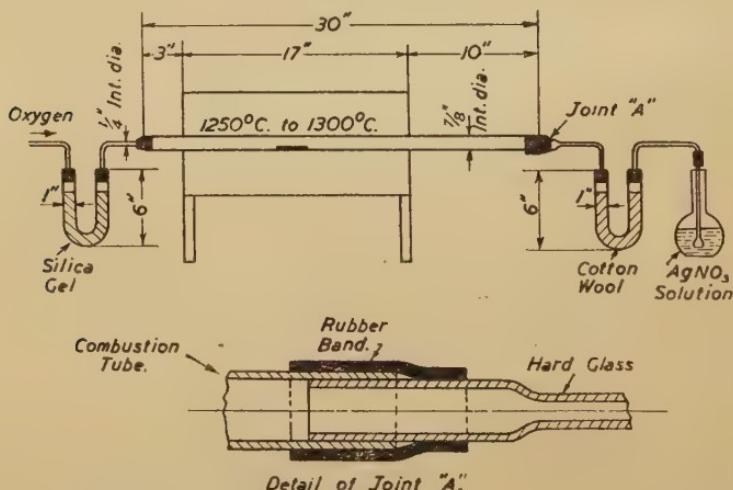


FIG. 4.—Apparatus for the Determination of Sulphur by Combustion.

### *The Combustion Tube.*

This consists of an unglazed porcelain tube, 30 in. long and  $\frac{7}{8}$  in. in internal diameter arranged in the furnace as shown. It is important that the tube project 10 in. from the furnace on the downstream side in order that the gas stream shall be cooled sufficiently before entering the cotton-wool filter. The special joint at the exit end of the tube is considered preferable to a rubber stopper, as overheating of the stopper is liable to give rise to volatile sulphur compounds which lead to high results. It is important to keep the tube clean and free from iron oxides, and it should therefore be scraped out after about 30 estimations. For work of the highest accuracy this procedure should be followed after each estimation. The full life of each tube is about 120–150 determinations. During the first few determinations with a new tube high results are frequently obtained, presumably owing to liberation of sulphur from the porcelain by the action of iron oxide. For this reason only seasoned tubes should be used for the most accurate work. When a tube is once in service low results are frequently obtained in the first run on heating up the tube after it has been allowed to cool.

### *The Furnace.*

Combustion should be carried out within the temperature range 1250–1300° C. Alternative heating elements which can be used to maintain this temperature are as follows :

(1) "*Silit*" Rods (for 110 V.).—Two at 8·7 ohms in parallel, with an external resistance of 2 to 0 ohms as the rods age, are suitable.

Two rods at 4·2 ohms in series may be used, but there is difficulty in maintaining the temperature, which becomes impossible when the rods age.

(2) "*Globar*" Elements.—Two rods (7 in. in effective length  $\times \frac{5}{16}$  in. in dia., 3·623 ohms) in series (690 watts) may be used.

If the voltage is higher than 110 V. it should be reduced to this figure with a transformer.

(3) *Platinum Windings*.—There are considerable advantages in using a platinum-wound furnace, as resistance rods are not easy to obtain and their current consumptions are very considerable. The initial cost of a platinum winding is somewhat offset by the high price obtainable for scrap platinum when a winding has to be replaced. A description of a platinum-wound furnace which has proved suitable is given in Appendix I.

### *The Oxygen Supply.*

Difficulties due to the carrying over of alkaline particles from a soda-lime drying tube have been experienced ; it is recommended that silica gel only be used for this purpose.

During the combustion period, a rapid stream of oxygen must

be maintained. A flow rate of 2·5–3 litres per min. is most suitable, and it is important that the rate should not fall below 2 litres per min. A flow gauge should be used for important work (see Appendix II.).

#### *The Filtering Medium.*

A filter is necessary to free the gas stream from iron oxides before passage through the absorbent. Cotton wool is most suitable for this purpose, and there is no danger of ignition if the combustion tube is arranged to project 10 in. from the furnace as recommended. Glass wool should not be used, as the capillaries which it contains may bring about adsorption of  $\text{SO}_2$  and lead to erratic results. For similar reasons it is essential that the cotton wool be perfectly dry and free from serious contamination by iron oxides. The first inch of cotton wool must therefore be replaced after each estimation for work of the highest accuracy. The cotton wool used should be dried at 105–110° C. in an oven reserved for the purpose and should not be touched by hand.

#### *The Absorbent.*

The  $\text{SO}_2$  is absorbed in 40 ml. of neutral N/50 silver nitrate solution containing methyl red as indicator. Many operators find it of advantage to add methylene blue to the indicator, as this gives a colour change which is more easy to detect by artificial light. The quantity of silver nitrate solution recommended may be used for six determinations in the case of samples with a sulphur content not exceeding 0·1%, this number being suitably decreased when the sulphur content is higher.

#### *The Titrating Agent and Standardisation.*

The nitric acid liberated should be titrated with approximately N/200 sodium hydroxide solution standardised against an iron or steel of known sulphur content. Care should be taken to wash out the delivery tube at the end of each titration.

#### *Procedure.*

One gramme of the iron (or 0·3 g. in the case of samples of high sulphur content) is placed in a porcelain boat, which is rapidly introduced into the hottest part of the combustion tube and the oxygen supply turned on. Titration is carried out during the combustion, the whole process occupying between 3½ and 4 min.

### THE DETERMINATION OF PHOSPHORUS IN PIG IRON.

As a preliminary step in the development of a standard method for the determination of phosphorus in pig iron, a series of three samples of hematite irons, containing about 0·02% of phosphorus, were analysed by members, using the method given in the British Cast Iron Research Association handbook "The Sampling and

Chemical Analysis of Cast Ferrous Metals," by E. Taylor-Austin. Results by this method and by members' own methods were not entirely satisfactory, a range of about 0·005% on 0·02% of phosphorus being obtained.

In discussion of the results fears were expressed as to the possible influence of arsenic on the determination. Silica, too, might be expected to interfere through contamination of the yellow precipitate by gelatinous silica and subsequent formation of silicomolybdates on solution with ammonia. On this account the method was modified to include an intermediate evaporation to render the silica insoluble. Members also contributed available informa-

TABLE II.—*Phosphorus Determinations in Pig Iron. Results obtained on two Samples by Different Methods in Various Laboratories.*

Analyst.	Sample 68; Phosphorus, %, by—		Sample 102; Phosphorus, %, by—	
	Method A.	Method B.	Method A.	Method B.
I.	0·021	<b>0·020</b>	<b>0·026</b>	<b>0·026</b>
II.	0·022	0·024	0·0305	0·031
III.	<i>0·024</i>	0·026	0·0305	<i>0·0325</i>
IV.	0·023	...	<i>0·031</i>	...
V.	0·022	0·0235	0·030	0·031
VI.	<i>0·024</i>	<i>0·0265</i>	0·030	<i>0·0325</i>
VII.	0·023	0·024	0·030	<i>0·0325</i>
VIII.	0·023	0·0255	...	0·027
Mean	0·0228	0·0242	0·0297	0·0303
Range	0·024	0·0265	0·031	0·0325
	{ 0·021	0·020	0·025	0·026
Difference	0·003	0·0065	0·005	0·0065
Mean error	0·0011	0·0022	0·0017	0·0027
Mean percentage error	4·8	9·1	3·7	8·9

NOTE.—High figures are italicised, low figures are in heavy type.

tion on the influence of temperature on the formation of the yellow precipitate. Experience generally indicated that the temperature after adding the precipitant should not exceed 75° C. The modified B.C.I.R.A. method thus arrived at is described under the heading "Method B" in Appendix III.

In connection with the problem of interference by arsenic, Dr. Gregory submitted a description of a method developed by the Standard Methods of Analysis Sub-Committee,<sup>1</sup> of which he is Chairman. This method, described under the heading "Method A", is designed to remove arsenic before precipitation of the phosphorus.

<sup>1</sup> *Journal of the Iron and Steel Institute*, 1942, No. I., p. 279 F.

Using the two methods referred to, members of the Sub-Committee carried out phosphorus determinations on two further samples (Nos. 68 and 102), with the results given in Table II.

It will be observed that method *A* has less than half the error associated with the second method. Sample 68 contained approximately 0·04% of arsenic, while sample 102 showed only a trace of the element. This suggests that the superiority of method *A* does not lie primarily in the removal of arsenic.

Before putting forward a recommended standard method, the Sub-Committee felt that some assurance was necessary as to the possible loss of phosphorus in the silica-graphite residue when appreciable amounts of titanium were present. Two further

TABLE III.—*Phosphorus Determinations in Pig Irons Containing Titanium.*

Analyst.	Phosphorus, %, in—					
	Sample B1.			Sample 38.		
	P. %.	ΔP. %.	ΣP. %.	P. %.	ΔP. %.	ΣP. %.
I.	0·033	0·0008	0·034	0·035	0·0010	0·036
II.	0·031	0·0015	0·0325	0·030	0·0015	0·0315
III.	0·032	0·0006	0·0325	0·0315	0·0006	0·032
IV.	0·031	Nil	0·031	0·032	Nil	0·032
V.	0·031	0·0003	0·0315	0·030	0·0005	0·0305
VII.	0·0305	0·0003	0·031	0·0295	0·0007	0·030
VIII.	0·032	0·0010	0·033	0·0295	0·0020	0·0315
Mean	0·0315	0·00064	0·0322	0·0311	0·0009	0·0319
Mean error	0·0009	...	0·0011	0·0020	...	0·0019
Mean percentage error	2·9	...	3·4	6·4	...	6·0

NOTE.—P = phosphorus by method *A*. ΔP = colorimetric phosphorus on residue. ΣP = total phosphorus.

samples, No. 38 containing 0·14% and No. B1 containing 0·17% of titanium, were circulated, and the phosphorus was determined by method *A*. In each case the phosphorus content of the residue was determined by a colorimetric method submitted by Mr. Westwood (*see Appendix III.*, method *C*), the results noted in Table III. being obtained.

In view of the fact that the presence of as much as 0·17% of titanium introduces an error of but 0·001% in the phosphorus determination, the Sub-Committee are of the opinion that interference from titanium may be neglected except in special cases where the highest accuracy is required. In these cases the colorimetric method *C* described in Appendix III. should be used to determine the loss of phosphorus in the silica-graphite residue.

For all normal cases it is recommended that method *A* be used.

**APPENDIX I.—*The Platinum-Wound Furnace.***

A fused alumina tube (Morgan  $\Delta V$ .67), 13 in. long,  $1\frac{1}{2}$  in. in dia. and  $1\frac{1}{4}$  in. bore, was coated to a depth of about  $\frac{1}{6}$  in. with alundum cement (Norton No. 562). Over an 8-in. length of this tube, 25 ft. of pure platinum wire, 0.010 in. in dia., was evenly wound. The winding was finally coated with alundum cement until the wire was completely covered. After careful drying, the wound tube was placed in a case, 12 in.  $\times$  12 in.  $\times$  12 in., and lagged by filling the case entirely with aluminous filling material (Morgan  $\Delta V$  alumina, No. 414).

Combustion is carried out in a "special  $\Delta H$ " tube (Morgan), 30 in. long and  $\frac{7}{8}$  in. bore. When the furnace is started from cold, the current consumption is about 6 amp., but this falls rapidly as the temperature rises. The maximum current at high temperatures is 2.7 amp.; it was found that 2.2 amp. will maintain a temperature of  $1350^{\circ}$  C. without undue drop when the combustion boat is introduced. The maximum temperature of the furnace is in excess of  $1550^{\circ}$  C. at 2.7 amp. If required, a temperature of  $1400^{\circ}$  C. can be attained in 45 min., but such a procedure is not recommended, owing to possible damage to the combustion tube.

These combustion tubes require careful treatment when first introduced into the furnace, if a reasonable life is to be obtained from them. The tube should be placed in the furnace, preferably when the latter is cold, but certainly when it is below red heat, and the temperature raised to about  $900^{\circ}$  C. in 2-3 hr., and to the working temperature of  $1300$ - $1350^{\circ}$  C. in, say, 4 hr. Subsequently the temperature should not be allowed to fall below  $600^{\circ}$  C.; when determinations are completed the current is cut down by means of a suitable resistance to about 1 amp., which maintains a temperature of about  $650$ - $700^{\circ}$  C. Thus the combustion tube, once heated, is kept at about  $600^{\circ}$  C. for the duration of its life. After the initial careful heating of the tube, its temperature is raised from the over-night figure of, say,  $650^{\circ}$  C. to  $1300^{\circ}$  C. in  $1$ - $1\frac{1}{2}$  hr.

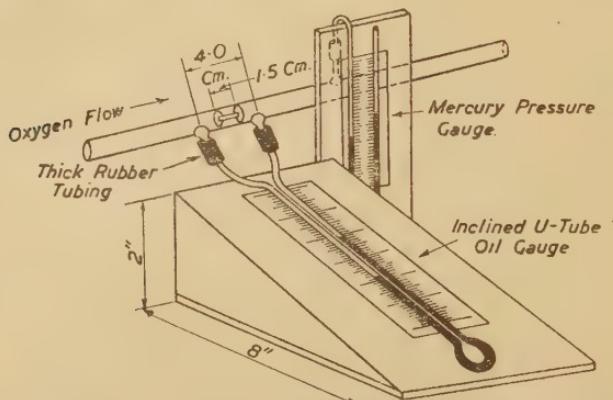
If the above precautions are observed, between 180 and 200 determinations can be made with each combustion tube.

**APPENDIX II.—*The Effect of the Rate of Oxygen Supply on the Determination of Sulphur by the Combustion Method.***

In order to control and measure the oxygen flow rate, two simple orifice gauges were constructed from glass tubing and mounted on inclined stands (slope about 1 in 4) and inserted in the system before and after the furnace. Figs. 5 and 6 show the details of the instruments. The orifices consisted of short lengths of glass tubing held in place by paraffin wax. The gauges were filled with a light mineral oil to give adequate sensitivity and to avoid the

introduction of water vapour, and calibration was carried out by direct comparison with a gas meter.

A series of experiments was first carried out to determine the



Orifice Details	Internal Diameter of Tube	Diameter of Orifice
250-2000 Ml. per Min.	0.6 Cm.	about 0.15 Cm
500-10,000 Ml. per Min.	0.6 Cm.	about 0.25 Cm

FIG. 5.—Flow Meter B (before the furnace).

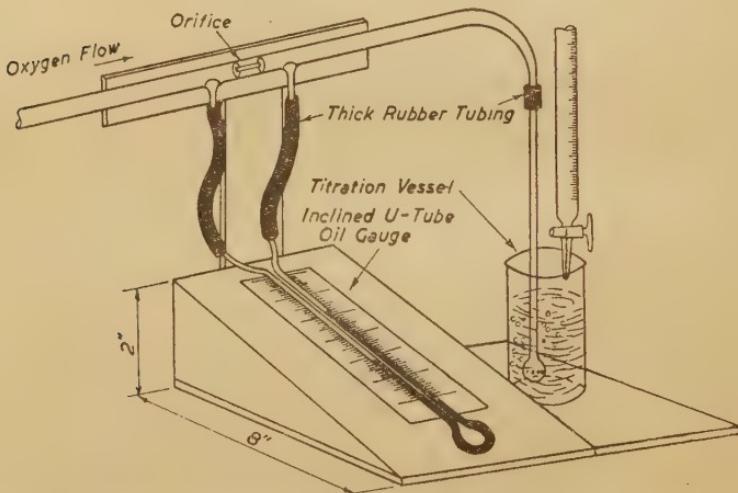


FIG. 6.—Flow Meter A (after the furnace). Orifice details as for meter B (Fig. 5).

"peak" value of the rate of oxygen supply to the furnace necessary to maintain a constant flow of oxygen through the final train. It was observed that the two gauges showed the same reading after 30-45 sec. The results are given in Table IV.

TABLE IV.—*Sulphur Determination by Combustion. Oxygen Supply Needed for Constant Flow in the Final Train.*

High-sulphur pig iron (0·163% of sulphur). Titrated after 3 min. End-point constant for further 2 min.

Temperature. ° C.	Oxygen, ml. per min., after Furnace.	Oxygen, ml. per min., "Peak" Value before Furnace during Combustion, approx.	N/200 NaOH. Ml.
1200	500	1100	13·7
1200	1000	1600	14·7
1200	1500	2200	15·8
1250	500	1400	13·8
1250	1000	1700	14·8
1250	1500	2000	16·1
1300	500	1400	13·7
1300	1000	1600	14·9
1300	1500	2500	15·85

A further series of experiments was carried out with a steady input of oxygen to the train to show the effect of varying this rate of flow on the results obtained; the data are reproduced in Table V. and Fig. 7.

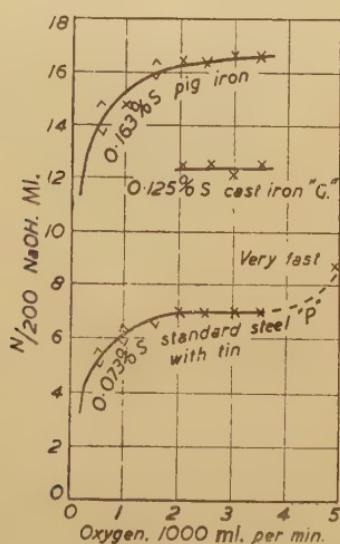


FIG. 7.—Effect of the Velocity of the Oxygen Stream on the Determination of Sulphur by Combustion.

TABLE V.—*Sulphur Determination by Combustion. Effect of Varying the Rate of Oxygen Flow.*

Sample.	Temperature. ° C.	Rate of Oxygen Supply. ml. per min.	$N/200$ NaOH. ml. required after 5 min.
0·073% sulphur standard steel with tin flux.	1250	2500	6·84
	1250	2500	6·89
	1250	3000	6·89
	1250	3000	6·79
	1250	3500	7·06
	1250	3500	6·96
0·125% sulphur standard cast iron (no flux).	1250	2500	12·4
	1250	2500	12·4
	1250	3000	12·2
	1250	3000	12·3
	1250	3500	12·5
	1250	3500	12·6
0·163% sulphur pig iron (no flux).	1280	3000	16·6
	1280	3500	16·6

APPENDIX III.—*Methods for the Determination of Phosphorus in Pig Iron.**Method A.**Reagents.*

*Molybdate Reagent.*—Make 100 g. of molybdic oxide ( $MoO_3$ ) into a paste with 240 ml. of water and then dissolve in 170 ml. of ammonium hydroxide (sp. gr. 0·880); the resulting solution is poured, with repeated shaking, into 1250 ml. of nitric acid (sp. gr. 1·20) containing 2 ml. of 2% microcosmic salt solution. This reagent is allowed to stand and must be filtered immediately before use.

*Ammonium Acetate Solution.*—This solution is made from glacial acetic acid by diluting one part with two of distilled water, followed by neutralisation with 0·880 sp. gr. ammonia. Finally, the solution is just acidified with acetic acid and kept as a stock solution.

*25% Ammonium Chloride Solution.*—Dissolve 25 g. of solid ammonium chloride crystals in 100 ml. of distilled water.

*4% Lead Acetate Solution.*—Dissolve 4 g. of solid crystals in 100 ml. of distilled water.

*Procedure.*

To 2 g. of clean drillings, contained in a 400-ml. conical beaker, add 25 ml. of nitric acid (sp. gr. 1·42), followed by 15 ml. of hydrochloric acid (sp. gr. 1·16) added cautiously.

When solution is complete, evaporate to dryness and bake at a temperature of about  $300^\circ$  C. for 20 min. Cool and take up with

40 ml. of hydrochloric acid (sp. gr. 1·16), boiling until a clear solution is obtained.

Add 20 ml. of distilled water and filter into a 400-ml. conical beaker, washing with 5% hydrochloric acid solution (5 ml. of acid of sp. gr. 1·16 in 100 ml. of water). The washing is conducted so as to keep the total bulk as low as possible.

Add 5 g. of ammonium bromide and, with the cover of the beaker removed, evaporate the solution until white fumes appear at the surface of the liquid. (The volume of the liquid at this stage is about 4 ml.)

Add 10 ml. of nitric acid (sp. gr. 1·42) and warm gently until the bromine is eliminated.

Dilute with 40 ml. of cold water and add ammonium hydroxide (sp. gr. 0·880) in slight excess (about 8 ml. will be required).

Just redissolve the precipitated ferric hydroxide by the cautious addition of 4–5 ml. of nitric acid (sp. gr. 1·42) and add 4 ml. in excess. Raise, or adjust, the temperature of the solution to 80° C. and add 35 ml. of the filtered molybdate reagent. Shake the solution until the precipitate forms and then allow to stand for 20 min.

Filter on an ashless paper-pulp pad, washing the precipitate from the beaker to the filter with cold dilute 2% nitric acid solution (2 ml. of nitric acid (sp. gr. 1·42) in 98 ml. of distilled water). Continue the washing of the pad and precipitate until these are free from iron salts. Usually, about six washes are sufficient for this purpose.

Transfer the funnel and filter to the neck of the original containing vessel and dissolve the yellow precipitate through the pad by the dropwise addition of 15 ml. of ammonium hydroxide solution (1 part of 0·880 sp. gr. ammonia diluted with 2 parts by volume of distilled water), finally washing the pad two or three times with hot water.

Refilter the ammoniacal extract, through the same filter, into a clean conical flask, washing this time thoroughly with hot water (at least ten washings with hot water are generally necessary). Place the flask containing the filtrate on the hot-plate, together with a second flask containing 50 ml. of ammonium acetate solution and 50 ml. of 25% ammonium chloride solution.

At boiling point add 10 ml. of hydrochloric acid (sp. gr. 1·16) to the ammoniacal extract, followed by 8 ml. of 4% lead acetate solution. If a precipitate forms, the solution is cleared by a further addition of hydrochloric acid, added dropwise. The contents of this flask are poured into the acetate-chloride solution, rinsing thoroughly with hot water.

Boil and then allow the precipitated lead molybdate to settle. Filter and collect the precipitate on an ashless paper or pulp-pad, wash thoroughly with hot water, and transfer the filter and precipitate to a clean tared porcelain crucible.

Dry and ignite, cautiously at first, and finally at a temperature not exceeding  $650^{\circ}$  C. Cool in a desiccator and weigh. The weight of the precipitate multiplied by 0.35 gives the percentage of phosphorus in the iron when 2 g. of the latter are initially weighed out.

### *Method B.*

#### *Reagents.*

*Ammonium Nitro-Molybdate.*—Moisten 125 g. of pure molybdic oxide with sufficient water to form a paste, add 100 ml. of ammonium hydroxide (sp. gr. 0.880), and shake vigorously until solution is complete. (It may be necessary to add a little more water after the addition of ammonium hydroxide in order to effect complete solution.) Dilute to 500 ml. with water and cool the solution to room temperature. Pour this solution slowly into 1,500 ml. of cold nitric acid (sp. gr. 1.2), keeping the mixture well agitated throughout. The mixing may conveniently be carried out by drawing a current of air through the solution, and this procedure should be continued for at least one hour after the addition of the ammonium molybdate solution. The requisite amount of solution for each batch of determinations should be filtered from this stock immediately before use. For the highest accuracy the molybdate solution should not be more than a week old.

*Lead Acetate.*—Dissolve 40 g. of lead acetate in distilled water, add sufficient 33% acetic acid to dissolve the precipitated lead compound and dilute to one litre.

#### *Procedure.*

Dissolve 0.5–2 g. of sample (depending on the amount of phosphorus present) in 45 ml. of nitric acid (sp. gr. 1.2), take carefully to dryness and bake. Cool, redissolve in concentrated hydrochloric acid with 1 ml. of concentrated nitric acid, take to dryness and bake to render the silica insoluble. Cool and take up in concentrated hydrochloric acid. Evaporate the solution almost to dryness to remove excess hydrochloric acid, add 25 ml. of nitric acid (sp. gr. 1.20), boil and filter off graphitic carbon. Bring the filtrate to the boil and add potassium permanganate solution (25 g. per litre) from a dropping bottle until a brown precipitate appears and persists during 3 min. continuous boiling. Remove from the hot-plate and add sufficient sulphurous acid to clear the solution; boil for a further 2–3 min., until the excess sulphur dioxide has been expelled. Allow the solution to cool somewhat and add 6 ml. of ammonium hydroxide. Adjust the temperature to about  $80^{\circ}$  C. and add 50 ml. of cold nitro-molybdate solution. Shake vigorously and allow to stand at about  $60^{\circ}$  C. until the yellow precipitate formed has settled and the solution above is clear (20 min.). Filter on a paper-pad filter and wash with cold 2% nitric acid until free from iron salts. Generally three washes will be sufficient.

Place the funnel containing the ammonium phospho-molybdate precipitate over the flask in which precipitation was carried out, pour 6 ml. of ammonium hydroxide (sp. gr. 0.880) round the funnel on to the pad and wash three times with hot water. Wash down the stem of the funnel and place under it a 400-ml. beaker; pour the ammoniacal solution containing the phosphorus back through the pad and wash the filter well with hot water.

Add 25–35 g. of ammonium chloride, depending upon the amount of phosphorus present. Render the solution just acid to litmus with 33% acetic acid and add 20 ml. in excess; boil and add 50 ml. of 4% lead acetate solution. Continue boiling for about one minute, filter and wash at least twelve times with hot 2% acetic acid. Ignite at a dull red heat, cool and weigh as lead molybdate.

$$\frac{\text{Weight of precipitate} \times 0.704}{\text{Weight of sample taken}} = \text{percentage of phosphorus.}$$

### *Method C.<sup>1</sup>*

#### *Reagents and Standard Solutions.*

*Ammonium-Molybdate/Sulphuric-Acid Solution.*—Dissolve 1 g. of ammonium molybdate in 100 ml. of distilled water, and to this solution add a cooled solution of 4.5 ml. of concentrated sulphuric acid in 100 ml. of distilled water. The mixture is diluted to one litre with distilled water.

*Stannous Chloride Solution.*—Weigh out 1 g. of pure tin and 0.025 g. of copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), add 20 ml. of concentrated hydrochloric acid and heat the mixture gently on the water-bath until effervescence has ceased. After cooling, about 20 ml. of distilled water are added and the solution is filtered, the filtrate being diluted to 100 ml. with distilled water. The solution is stored in a stoppered flask and protected from light.

*Gum Acacia Solution.*—A 1% solution of gum acacia in distilled water is prepared, using distilled water at 50° C. and cooling when solution is complete.

*Standard Solutions of Sodium Phosphate.*—(a) *Concentrated solution*: 2.29 g. of anhydrous sodium phosphate,  $\text{Na}_2\text{HPO}_4$ , are dissolved in one litre of distilled water. 1 ml. = 0.0005 g. of phosphorus. (b) *Dilute solution*: Dilute 10 ml. of the concentrated solution to one litre with distilled water; 1 ml. = 0.000005 g. of phosphorus.

#### *Procedure.*

The residue of graphite and silica obtained from the phosphorus determination is ignited in a platinum crucible, treated with hydrofluoric acid to remove silica, and then fused with 1 g. of sodium

<sup>1</sup> Adapted from N. T. Wilkinson, "The Colorimetric Determination of Phosphate in Boiler Water," *Journal of the Society of Chemical Industry*, 1938, vol. 57, p. 292.

carbonate. The fusion is extracted in 50 ml. of 10% sulphuric acid and the volume of the solution adjusted to 100 ml.; 50 ml. of solution are pipetted off, 5 ml. of gum acacia are added and the solution is made faintly ammoniacal. The solution is then boiled until all traces of ammonia have been expelled. After cooling, 5 ml. of the ammonium-molybdate/sulphuric-acid reagent are added and the solution is diluted to 100 ml. with distilled water. After thorough mixing, 0·1 ml. of stannous chloride reagent is added, and after further stirring the blue colour obtained is matched against a series of standards prepared from sodium phosphate solution. These standards contain 0·000002–0·00001 g. of phosphorus and are prepared by dissolving 1 g. of sodium carbonate in 50 ml. of 10% sulphuric acid, adding the required volume of standard dilute sodium phosphate solution and treating exactly as described above.

The reagents must be added in accurately measured amounts; a slight excess of molybdate increases the depth of blue colour produced, and excess of acid or alkali causes the colour to be less intense.

If much iron is present in the residue it can be removed after the extraction in sulphuric acid by precipitation with cupferron, the filtrate then being evaporated to low bulk with nitric acid to destroy the cupferron, diluted to 100 ml., and 50 ml. pipetted off for treatment as above.

#### CORRESPONDENCE.

Mr. C. R. TOTTLE (The English Electric Co., Ltd., Rugby) wrote : The combustion method of sulphur determination has been in regular use in the metallurgical laboratory of the writer's Company for pig irons, high-duty cast irons and steels with excellent results over a long period. The apparatus used was based on the suggestions of The British Cast Iron Research Association, with minor modifications.

The furnace used is a proprietary brand fitted with " Sunvic " control and employing a platinum winding. No difficulties have been experienced with this type of furnace, which is particularly convenient in maintaining temperatures at a constant level, with especial reference to the " stand-by " temperature of the Morgan  $\Delta H$  combustion tubes when not in use.

A flowmeter has been proved necessary to maintain a steady flow of oxygen, and the absorption of the sulphur dioxide is carried out in a specially designed vessel, details of the shape and size of which are given in Fig. A. The sintered-glass disc has been proved to give perfect absorption, and is extremely simple to use when washing out the delivery tube during the final period of titration. In conjunction with this absorption vessel, an automatic

filling burette assists in shortening the time required for one estimation, an average of 3 min. being maintained. Splashing of the absorbent during the evolution is not excessive with the sintered-glass disc, and six determinations can be readily accommodated before splashing is likely to cause error.

The cotton-wool filter has been invariably accommodated in a hard-glass prolong tube jointed to the combustion tube in the manner illustrated in Fig. 4 of the paper, thus providing easy removal of the cotton wool between each estimation, and eliminating the U-tube between the combustion tube and the absorption vessel. Ignition of the cotton-wool filter has never occurred with a 10-in. projection of the combustion tube from the furnace.

Mr. A. ALLISON (Messrs. J. J. Habershon & Sons, Ltd., Rotherham) wrote : The work of the Sub-Committee on the estimation of sulphur by combustion shows reasonable agreement in view of the small weight taken for analysis of a variable material. I think even better results would be obtained if it were feasible to work on 2 g.

In laboratories where the volume of work does not justify the installation of combustion apparatus, I consider that the gravimetric method would be satisfactory, provided that attention were given to two points :

(1) Instead of adding 1 g. of barium chloride as formerly advised, add 2 g. to overcome the solubility of barium sulphate in hydrochloric acid.

(2) With low-sulphur irons add an artificial blank by means of a measured amount of sulphate.

The phosphorus methods would, I think, show closer agreement by starting with 5 g. and then taking an aliquot part of the solution obtained, for precipitation. With pig irons and cast irons it is not

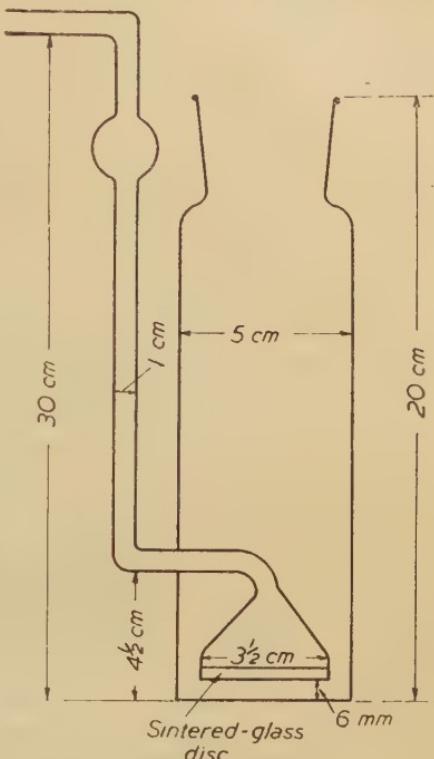


FIG. A.—Absorption Vessel for the Combustion Method of Sulphur Determination.

easy to weigh out a fair sample, and in method *B* I should never agree to take only 0.5 g. of phosphoric-iron samples.

The Sub-Committee found that method *A* gave results more closely agreeing, and I think that the explanation is that the solution is rendered alkaline with ammonia and then acidified with nitric acid before precipitating. I have generally noticed a sharper precipitation after taking down to dryness, taking up with hydrochloric acid, adding ammonia till alkaline and then adding excess of nitric acid. Possibly the extra ammonium salts produced the better precipitation.

It will be noticed that methods *A* and *B* are chemically inconsistent. In method *A* the solution is evaporated and baked once without further oxidation. In method *B* the solution is evaporated and baked twice, and then subsequently oxidised with permanganate. It has always been understood that evaporation and baking ensure the oxidation to orthophosphoric acid.

The information about the negligible interference of titanium is useful, and, since phosphoric irons generally contain up to 0.2% of vanadium in addition to titanium, it is worth while adding sulphurous acid to avoid interference by the former.

The volumetric finish, which I prefer, raises the question of absolute standards for phosphorus, and I would suggest that by taking reagents of guaranteed purity—anhydrous potassium phosphate, hydrated sodium phosphate and microcosmic salt—comparison would show reliable standards by agreement. If solutions were prepared from all three, such that 20 ml. = 0.001 g. of phosphorus = 0.05% on 2 g., this quantity could be precipitated after addition of nitric acid and ammonium nitrate, and duplicate precipitates used for standardising the soda solution, and also for translation into lead molybdate; moreover, the solution could be examined in any other manner thought to be desirable.

In committee work of this nature would it not be useful for high-result operators and low-result operators to exchange visits?

Mr. C. DINSDALE (London and North Eastern Railway Co., Doncaster) wrote: For the determination of sulphur in pig iron (the same method can presumably be applied to cast iron) the Sub-Committee have recommended the combustion method. In the writer's opinion there are two objections to this.

First, many laboratories which are not asked to analyse many samples of pig iron would not be able to justify an expenditure of some £40 or so on the necessary high-temperature platinum-wound furnace and its accessories. From the remarks on pp. 305 P and 309 P intermittent working of the furnace does not seem desirable.

Secondly, the weakness of the proposed combustion method as a standard method is admitted on p. 303 P to be the difficulty of standardisation of the *N*/200 sodium hydroxide titrating solution. This necessitates comparison with an iron or steel sample of known

sulphur content. As the combustion method was not considered suitable for referee determinations of sulphur in steel<sup>1</sup> such procedure cannot be regarded as a satisfactory standard method.

The Sub-Committee have found difficulty in controlling the gravimetric determination of the sulphur in low-sulphur hematite irons; was the device used in the standard method (*loc. cit.*) for sulphur in steel tried, *i.e.*, the addition of a known amount of potassium sulphate?

The results obtained by the standardised combustion method on sample A and given in Table I. do not compare very favourably with those obtained by the aqua-regia gravimetric method on the steel G (*loc. cit.*).

The determination of phosphorus seems to have been limited to its estimation in hematite iron. Do the Sub-Committee suggest that the weight of sample and volumes of solutions given in the recommended method A are applicable both to hematite irons containing, say, 0·02% of phosphorus and to phosphoric irons with 1·5%?

#### SUB-COMMITTEE'S REPLY.

The SUB-COMMITTEE, in reply, wish to thank the contributors to the discussion for the interest expressed.

With regard to the special absorption vessel described by Mr. Tottle, the Sub-Committee would point out that it has found no reason to suspect imperfect absorption in its work. On the other hand, it is considered that the sintered-glass disc will inevitably retain sulphur gases in solution within the capillaries, thereby giving low initial results and erratic results in subsequent determinations.

The Sub-Committee are in complete agreement with Mr. Allison regarding the advantages of method A; it is well known that the precipitation of phospho-molybdate is retarded in the presence of chlorides and accelerated by ammonium nitrate. The Sub-Committee cannot, however, accept the view that the two methods are "chemically inconsistent." The second evaporation with hydrochloric acid and subsequent oxidation with potassium permanganate, embodied in the method, are precautions against possible contamination by silica and incomplete oxidation, respectively. As the Sub-Committee found that normally these additional refinements were unnecessary, they recommended the use of method A.

Mr. Allison's suggestion for the exchange of visits between operators reporting high and low results, respectively, is to be commended and the Sub-Committee hope to arrange facilities for this in the future.

The Sub-Committee, while sympathising with Mr. Dinsdale on

<sup>1</sup> First Report of the Standard Methods of Analysis Sub-Committee, *Journal of The Iron and Steel Institute*, 1942, No. I., p. 279 P.

the subject of the cost of apparatus, would point out that the expenditure mentioned can be cut down to about one-fifth if the combustion furnace is made in the laboratory. If one of the proprietary carborundum-type resistance rods is used, a satisfactory furnace can be made up for a few pounds.

With regard to Mr. Dinsdale's last point, the Sub-Committee would not recommend the use of method *A* where the phosphorus content of the sample is in excess of 0·1%. In method *B*, moreover, double precipitation of the lead molybdate is desirable if the phosphorus content exceeds 0·4%. The question of the determination of phosphorus in high-phosphorus materials is under consideration, and it is regretted that the limitations in this respect were not made clear in the paper.

# RIMMING STEEL.—EXPERIMENTS ON MELTS OF RIMMING-STEEL COMPOSITION IN THE LABORATORY HIGH-FREQUENCY FURNACE.<sup>1</sup>

BY T. SWINDEN, D.MET., W. W. STEVENSON, F.I.C., A.M.I.CHEM.E., AND G. E. SPEIGHT, B.Sc., A.I.C. (CENTRAL RESEARCH DEPARTMENT, THE UNITED STEEL COMPANIES, LTD., STOCKSBIDGE, NEAR SHEFFIELD).

(Figs. 2 to 7 = Plates XVIII. to XXIII.)

*Paper No. 28/1944 of the Committee on the Heterogeneity of Steel Ingots.)*

## SUMMARY.

Using a small high-frequency melting unit (nominal capacity, 18 lb. of metal), experiments were conducted in an endeavour to reproduce the conditions prevailing during the freezing of commercial rimming-steel ingots. Owing to the small mass of material involved this was not completely possible, but some interesting observations were made. A noticeable feature was the invariable appearance of a thick crust of pure "rim" at the top of the ingots.

## INTRODUCTION.

In a recent paper by Mitchell<sup>2</sup> the effect of different mould size on the degree of effervescence, using the same class of steel, was demonstrated in an interesting manner. Further large-scale practical investigations of this type are highly desirable to provide information by which the exhaustive theoretical hypotheses now existent concerning rimming steel can be judged.

It was thought that if large-scale practice could be simulated in a small furnace by applying controlled rates of cooling, this might indicate the directions in which large-scale experiments could best be pursued, as, for example, the investigation of the influence of mould temperature, mould/ingot weight ratio, ingot dimensions, &c.

It was with this object in mind that the experiments now described were carried out, but, unfortunately, although the rate of cooling could be controlled, it was not found possible to produce a small ingot in this way which really represented a good commercial rimming-steel ingot. Nevertheless, the results are, it is thought, of sufficient interest to warrant publication. As described later,

<sup>1</sup> Received January 7, 1944. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed are the authors', and are not necessarily endorsed by the Committee as a body.

<sup>2</sup> *Journal of The Iron and Steel Institute*, 1942, No. II., p. 327 p.  
1944—i

the desired rate of cooling was obtained by allowing the steel to solidify in the crucible under controlled conditions, and the authors were successful in many cases in securing "effervescence" which lasted for several minutes.

### EXPERIMENTAL TECHNIQUE.

The method of melting was as follows: A charge, weighing 6000 g. and composed of ingot iron and high-carbon iron, was melted in a magnesite crucible. When molten, an addition of high-carbon ferro-manganese (and, in certain cases, ferro-phosphorus) was made, the power input was stabilised at 15–16 kW. and the melt allowed to stand for 5 min., following which the temperature was taken by the immersion pyrometer. In the two final experiments (*SG. Nos. 4729 and 4730*) small samples of the liquid steel were taken at this stage, by a modified bomb technique,<sup>1</sup> for determination of carbon by combustion and oxygen by vacuum fusion.

Solidification of the molten steel was allowed to proceed in the crucible used for melting it. The following four methods of cooling were used during the course of the experiments, these being designated *A, B, C* and *D*, in Table I.:

*Method A.*—After stabilising at 15–16 kW., the power input to the furnace was switched off and the melt allowed to cool in the open crucible. This method made possible good observation of the freezing, but was considered to lead to undue chilling of the surface and early crust formation.

*Method B.*—To overcome the above defect, a closely fitting plug, made from a refractory brick, was inserted into the crucible during the stabilising period, after which the power input to the furnace was cut off. Fig. 1 shows the arrangement of crucible and refractory plug.

*Method C.*—To decrease still further the rate of cooling, the power input to the furnace was reduced to 5 kW. and solidification allowed to proceed under the refractory plug. This method, together with the following method *D*, which was substantially similar, increased the time of cooling.

*Method D.*—After insertion of the refractory plug, the power to the furnace was gradually decreased from 16 kW. to 5 kW. over a period of 10 min. and maintained at 5 kW. until 5 min. after solidification of the crust.

Table I. gives the results of these experiments, together with steelmaking details, including the composition and analysis of the charge, progress of freezing, &c.

The tendency towards excessive crust formation rendered observations and comparison with the true rimming action difficult,

<sup>1</sup> Swinden and Stevenson, Fourth Report of The Oxygen Sub-Committee, *Journal of The Iron and Steel Institute*, 1943, No. II., p. 397 p.

but in all cases there was an evolution of gas, which burned with a pale blue flame and was, presumably, carbon monoxide. Just

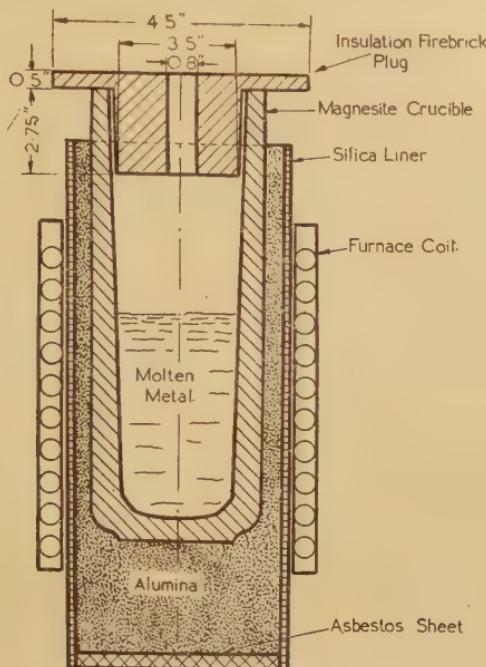


FIG. 1.—Section through Centre of Spark-Gap Furnace fitted with Firebrick Plug.

before the surface crusted over there was, in most cases, a slight effervescence where the evolved gas burst through the pasty covering. In several experiments the crucible was found subsequently to be cracked just below the level of the solidified crust, and metal had penetrated the crack; this effect was strongly indicative of a severe gas pressure.

#### METALLURGICAL EXAMINATION.

The small ingots so produced were sectioned longitudinally and examined by sulphur-printing and macro-etching. The sulphur prints and macro-etched surfaces of a few of these ingots are reproduced in Figs. 3 to 8, respectively.

#### CHEMICAL ANALYSIS.

A selection of six ingots was subjected to chemical analysis at four or five specified positions in the longitudinal section. From the interior of the sections, drillings were taken with a  $\frac{1}{2}$ -in. drill to a depth of  $\frac{1}{2}$  in.; from the edge portions millings were obtained.

TABLE I.—*Rimming-Steel Experiments*

Crucible, basic. Weight

Analyses of

			C. %.	Mn. %.	Si. %.	S. %.	P. %.
Ingot iron . . . . .	. . . . .	. . . . .	0.03 <sub>4</sub>	0.09	Trace	0.022	0.006
High-carbon iron . . . . .	. . . . .	. . . . .	3.60	0.2	0.3	0.01	0.035

SG. No.	Composition of Charge. G.				Analysis of Charge. %.			
	Ingot Iron.	High-Carbon Iron.	High-Carbon Fe-Mn.	Fe-P.	C.	Mn.	S.	P.
4630	5500	460	40	...	0.33 <sub>5</sub>	0.51	0.022	0.010
4629	5630	350	40 <sup>c</sup>	...	0.27	0.51	0.022	0.009 <sub>5</sub>
4515	5630	330	39	...	0.26	0.50	0.022	0.009 <sub>5</sub>
4516	5630	330	39	...	0.26	0.50	0.022	0.009 <sub>5</sub>
4702	5617	350	30	3	0.26	0.39	0.022	0.023
4687	5640	330	30	...	0.25	0.39	0.022	0.009
4706	5667	300	30	3	0.23	0.39	0.022	0.023
4688	5690	280	30	...	0.21 <sub>5</sub>	0.39	0.022	0.009
4701	5717	250	30	3	0.20	0.39	0.022	0.022
4686	5740	230	30	...	0.18 <sub>5</sub>	0.39	0.022	0.008 <sub>5</sub>
4705	5767	200	30	3	0.17	0.39	0.022	0.022
4729	5772	200	25	3	0.16 <sub>5</sub>	0.32	0.022	0.022
4730	5822	150	25	3	0.13 <sub>5</sub>	0.32	0.022	0.022

\* Methods of cooling described under

*in Laboratory High-Frequency Furnace.*

of charge, 6000 g.

base materials :

High-carbon Fe-Mn Ferro-phosphorus	:	:	O. %.	Mn. %.	Si. %.	S. %.	P. %.
			6.30	76.0	1.55	0.028	0.174
			...	...	...	...	28.0

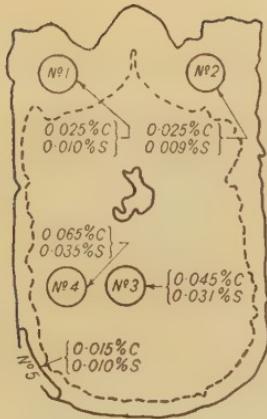
Freezing of Melt.				Degree of Rimming.		Remarks.
Temp. ° C.	Method of Cooling.*	Time to Formation of Crust. Min.	Weight of Alumin- ium. G.	Base.	Wall $\frac{2}{3}$ from Base.	
1605	B	6	Nil	No evidence of rimming.		Heavy central segregation. Large blow-hole formation to edges. Ingot rose towards end of solidifi- cation.
1610	B	5	Nil	Slight evidence of rimming.		Heavy central segregation. Large blow-hole formation in central zone. Ingot rose.
1600	A	9	0.2 g. (0.003%)	Slight rimming. 0.2 in.   0.25 in.		Fairly uniform homogeneity in central zone. Small blow-hole formation near rim-core junction. Analysis at selected positions.
1580	A	8	0.5 g. (0.008%)	Slight rimming. 0.15 in.   0.25 in.		Uniform central zone. Very small blow-hole formation in centre and near junction. Analysis at selected positions.
1650	B	5	Nil	No evidence of rimming.		Uniform structure and compo- sition. A few large blow-holes in upper half.
1570	B	5	Nil	Slight rimming. 0.1 in.   0.2-0.25 in.		Fairly uniform central zone. Large blow-holes in central zone.
1644	C	10	Nil	Very slight rimming.		Large central blow-hole (crucible cracked, probably owing to gas pressure). Blow-hole formation to centre.
...	B	4	Nil	Marked rimming. 0.45 in.   0.55 in.		Large central blow-hole forma- tion. Evidence of double rim, crucible cracked probably by gas pressure, and metal ran out. Analysis at selected positions.
1630	B	3½	Nil	Slight rimming. 0.25 in.   0.25 in.		Small blow-hole formation near rim-core junction. Uniform central zone.
1592	B	7½	0.2 g. (0.003%)	Marked rimming. 0.25 in.   0.45 in.		Uniform central zone. Small blow-hole formation. Analysis at selected positions.
1644	C	9	Nil	Marked rimming. 0.3 in.   0.3 in.		Small blow-hole formation in upper half. Uniform central zone.
...	D	8 min. at 5 kW.	Nil	Marked rimming. 0.55 in.   0.75 in.		1 large blow-hole in upper half. Blow-hole formation small. Uniform central zone. Crucible cracked. Analysis at selected positions.
...	D	6 min. at 5 kW.	Nil	Marked rimming. 0.3 in.   0.35 in.		Blow-hole formation very small. Uniform central zone. Analysis at selected positions.

" Experimental Technique."

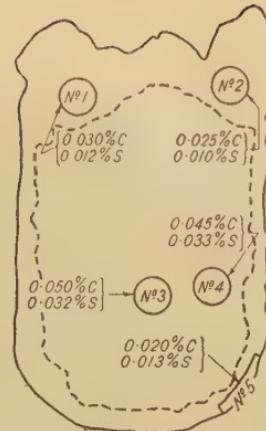
TABLE II.—*Compositions of Samples Taken from Specified Positions in Sections of SG. Ingots.*

The numbered positions in the ingots are indicated in Fig. 2.

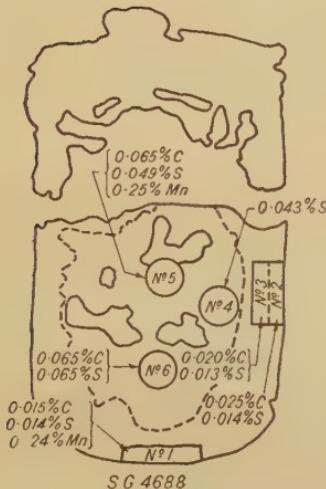
Position of Sample.	C. %.	S. %.	
<i>SG. 4515.</i>			
1. Rim, upper crust . . . . .	0.025	0.010	
2. Rim, upper crust . . . . .	0.025	0.009	
3. Core, centre of ingot . . . . .	0.045	0.031	
4. Core, midway between centre and junction . . . . .	0.065	0.035	
5. Rim, bottom corner . . . . .	0.015	0.010	
<i>SG. 4516.</i>			
1. Rim, upper crust . . . . .	0.030	0.012	
2. Rim, upper crust . . . . .	0.025	0.010	
3. Core, centre of ingot . . . . .	0.050	0.032	
4. Core, midway between centre and junction . . . . .	0.045	0.033	
5. Rim, bottom corner . . . . .	0.020	0.013	
	C. %.	Mn. %.	
<i>SG. 4688.</i>			
1. Rim, base, outer 0.25 in. . . . .	0.015	0.24	0.014
2. Rim, midpoint, outer 0.25 in., 1st cut . . . . .	0.025	...	0.014
3. Rim, midpoint, inner 0.2 in., 2nd cut . . . . .	0.020	...	0.013
4. Core, midpoint between centre and edge . . . . .	...	...	0.043
5. Core, centre of ingot . . . . .	0.065	0.25	0.049
6. Core, midway between base and position 5 . . . . .	0.065	...	0.065
	C. %.	S. %.	O <sub>2</sub> . %.
<i>SG. 4686.</i>			
1. Rim, base, outer 0.375 in. . . . .	0.010	0.24 <sub>5</sub>	0.015
2. Core, centre axis, midway between centre and base . . . . .	0.035	0.25	0.040
3. Rim, midpoint, outer 0.375 in. . . . .	0.020	...	0.014
4. Core, midway between centre and position 3 . . . . .	0.035	...	0.039
	C. %.	S. %.	O <sub>2</sub> . %.
<i>SG. 4729.</i>			
Test-bit sample before solidification of ingot	0.055	...	0.058
1. Rim, base, outer 0.375 in. . . . .	0.015	0.019	...
2. Rim, middle of ingot, outer 0.375 in. . . . .	0.010	0.021	0.053
3. Core, central axis, middle of ingot . . . . .	0.030	0.061	...
4. Core, midway between positions 2 and 3 . . . . .	0.040	0.060	...
5. Core, midway between positions 1 and 3 . . . . .	0.020	0.039	...
6. Core, adjacent to position 5 . . . . .	...	...	0.054
	C. %.	S. %.	O <sub>2</sub> . %.
<i>SG. 4730.</i>			
Test-bit sample before solidification of ingot	0.035	...	0.072
1. Rim, base, outer $\frac{1}{2}$ – $\frac{3}{16}$ in. . . . .	0.010	0.015	...
2. Rim, middle of ingot, outer 0.2 in. . . . .	0.020	0.014	...
3. Core, central axis, middle of ingot . . . . .	0.020	0.042	...
4. Core, midway between position 3 and edge . . . . .	0.040	0.034	...
5. Core, central axis, just inside core . . . . .	0.020	0.041	...



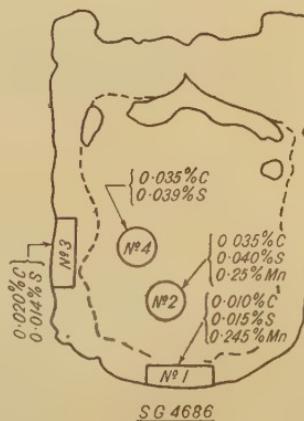
SG 4515



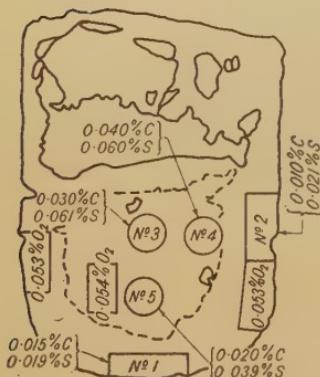
SG 4516



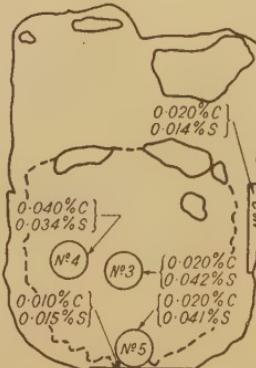
SG 4688



SG 4686



SG 4729



SG 4730

FIG. 2.—Analysis of Specified Positions in SG Rimming Ingots.

The positions sampled corresponded to several rim and core positions. Carbon and sulphur determinations were carried out on each sample and, in addition, manganese determinations were made on several of the samples. Oxygen determinations by the vacuum fusion method were carried out at two positions, corresponding to the rim and core, in one of the later ingots (*SG.* 4729). Table II. gives the analytical results and Fig. 2 shows the positions of sampling and the analytical results diagrammatically.

#### COMMENTS.

(1) Evidence of the typical rimming-steel characteristic, *i.e.*, a sharp rim-core junction, is clearly evident in the sulphur print and macro-etch of nine of the steels examined. The most clearly marked and thickest rim zones occur in steels *SG.* 4688 and 4729, which contained respectively 0·21<sub>5</sub>% and 0·16<sub>5</sub>% of carbon in the charge. In these experiments rimming was obtained from charges having a maximum of 0·26% of carbon, although, had the more marked cooling rate been applied to charges of higher carbon content, this limit might conceivably have extended even higher.

(2) Control of the temperature of melting even under standardised conditions was difficult, as shown by the variations recorded in Table I. Temperatures of 1610° C. were regarded as optimum, but it was considered unnecessary at this stage to attempt closer adjustment of the temperature after melting, in view of the possible time required to ensure equilibrium. In these experiments the temperature of the melt before allowing it to cool appears to have little influence on the depth and extent of the rimming action.

(3) Blow-hole formation was, in general, irregular. All ingots, except those which were aluminium-treated during freezing, show a large cavity below the upper crust, due undoubtedly to the accumulation of gas from the freezing pasty metal. In certain cases, notably *SG.* Nos. 4629, 4516, 4687, 4706 and 4688, the core zone is irregularly spaced with blow-hole cavities, whilst in others (Nos. 4515, 4701, 4686 and 4729) blow-hole formation is mainly adjacent to the rim-core junction. Other ingots, including *SG.* 4702, which is of non-rimming structure, and *SG.* Nos. 4705 and 4730, contain blow-holes only in the upper parts of the core zone.

(4) The chemical analysis confirms the sulphur-print evidence, in that the rim envelope is of more pure composition than the core zone, as regards both carbon and sulphur contents. Marked differences in sulphur content occur between the rim and core, whilst the differences in carbon are not so marked. The carbon values of both the rim and core of all the ingots are of an exceedingly low order, which, in view of the carbon content charged, indicates a rather heavy loss of carbon during the melting-down period. The loss of carbon during melting is shown also by *SG.* 4729 and 4730, which gave samples at melting of 0·055 and 0·035% of carbon, respectively,

PLATE XVIII.



FIG. 3B.—SG. 4515. Macro-etch.



FIG. 3A.—SG. 4515. Sulphur Print.

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PLATE XIX.



FIG. 4B.—SG. 4516. Macro-etch.



FIG. 4A.—SG. 4516. Sulphur Print.

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PLATE XX.



FIG. 5B.—SG. 4688. Macro-etch.



FIG. 5A.—SG. 4688. Sulphur Print.

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PLATE XXI.

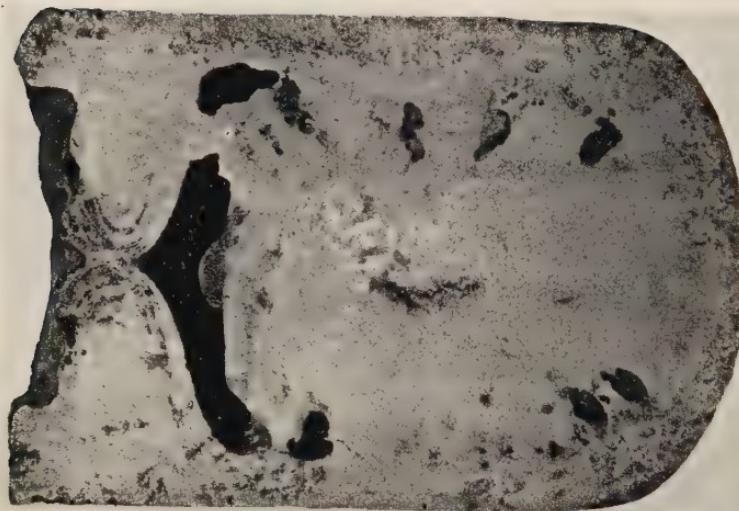


FIG. 6B.—*SG*, 4686. Macro-etch.



FIG. 6A.—*SG*, 4686. Sulphur Print.

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PLATE XXII.



FIG. 7B.—SG. 4729. Macro-etch.



FIG. 7A.—SG. 4729. Sulphur Print.

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PLATE XXIII.



FIG. 8B.—*SG. 4730*, Macro-etch.

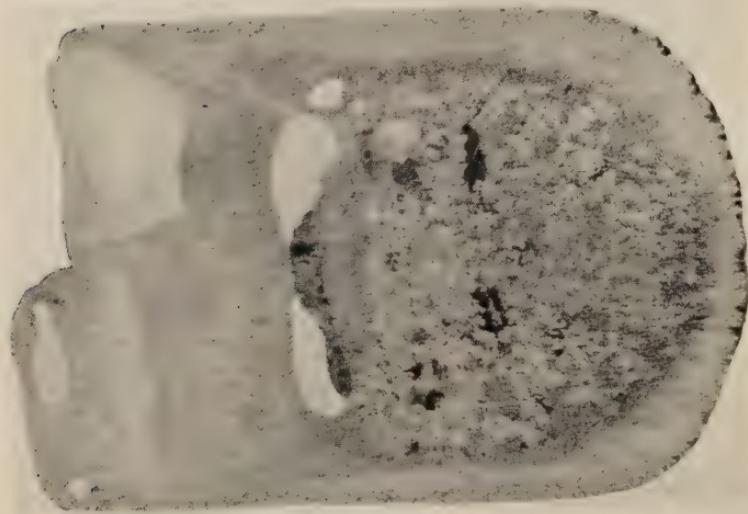


FIG. 8A.—*SG. 4730*, Sulphur Print.

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indicating a loss of 0·10% approximately. It is obvious that those charges having higher carbon contents suffered an even greater loss of carbon during melting down, although it had been hoped with higher-carbon charges to produce rimming steels of higher carbon contents.

(5) The two final ingots, *SG.* 4729 and 4730, were examined for carbon and oxygen by sampling before allowing them to cool. The steel with the lower carbon content, *i.e.*, *SG.* 4730, contains the higher oxygen, although the reaction products (*C*)  $\times$  (*O*) are not completely uniform, varying between 0·0032 and 0·0025, the lower reaction product being associated with the lower carbon content. However, it must be appreciated that slight deviations in the carbon figures at these low contents exert large effects on the calculated value of the reaction product.

(6) The effect of aluminium in these experimental melts is very marked, in that the freezing metal is partially quietened and gas evolution reduced. Consequently, the formation of crust, which grows owing to the splashing of metal on to it, is retarded and the freezing time thereby lengthened and the rim thickness increased. Moreover, the frequency of blow-holes in the core tends to be decreased. The judicious use of aluminium in these experiments may be said to have been equal to a reduction in the rate of solidification.

(7) The prime difficulty in reproducing ideal rimming conditions in these small ingots by the technique described above was the prevention of the rapid growth of the crust of pure metal. Indeed, the mechanism of the freezing of these ingots may be represented as follows :

Owing to the low reserve of heat in these small melts, solidification commences almost immediately at the liquid surface and a crust grows inwards from the crucible walls. As the liquid metal below cools, gas is evolved and metal tends to be splashed on to the growing crust, which thereby increases in area at the same time as the rim wall thickness increases, until complete crusting-over occurs. The gas evolved from the still liquid metal then increases in pressure, ultimately stopping the rimming action. Evidence for this is afforded by *SG.* 4688 and 4729, which show the deepest rim zones and also traces of double rimming, which presumably started again on release of the gas pressure consequent upon the cracking of the crucible. Crust formation in these experiments thus behaved in a similar manner to the cooler plate in normal rimming-steel practice.

(8) It is, with regret, concluded that this method of experimentation is not under sufficiently good control to permit of further work along the lines originally designed. It is submitted that the observations recorded here, whilst not adding to our fundamental knowledge of rimming steel, have certain interesting features.

One of these is the thick cap or crust of pure metal found at the top of all these ingots. It will be remembered that considerable

discussion has taken place concerning the existence of a thick rim of this type found on certain ingots of foreign origin.<sup>1</sup> There is little doubt, in the authors' view, that the explanation is similar to that applying to the small ingots now described. The thick cap of pure metal results from a chilling-over of the surface, which collects the comparatively pure metal being ejected from the effervescing surface of the steel during solidification.

The authors express their thanks to the Directors of The United Steel Companies, Ltd., for their permission to publish the results of these experiments.

<sup>1</sup> Examples 63 and 64 (from Denain), Sixth Report on the Heterogeneity of Steel Ingots, p. 40, *The Iron and Steel Institute*, 1935, *Special Report No. 9*.

# RIMMING STEEL.—AN EXAMINATION OF THE CARBON AND OXYGEN RELATIONSHIP IN THE SOLIDIFICATION OF BASIC OPEN-HEARTH STEEL.\*

By T. SWINDEN, D.Met., W. W. STEVENSON, F.I.C., A.M.I.Chem.E., AND G. E. SPEIGHT, B.Sc., A.I.C. (THE UNITED STEEL COMPANIES, LTD., STOCKSBRIDGE, NEAR SHEFFIELD).

(Figs. 1 to 6 = Plates XXIV. to XXVI.)

*Paper No. 24/1943 of the Committee on the Heterogeneity of Steel Ingots.*

## SUMMARY.

Recent papers to The Iron and Steel Institute on the examination of rimming steels are discussed in the light of the "balanced" composition hypothesis of Hultgren and Phragmén. Comments are made on the effects of manganese and pressure on the value of the balanced composition, and it is suggested that, owing to the effects of pressure, a single balanced composition does not exist for all parts of the same freezing ingot. Experimental work consisted of the sampling and examination of five casts of rimming steel, in the range of pit sample carbon analyses 0·04–0·14%. Calculated from the carbon and oxygen contents of the carefully prepared pit samples, the product (O)  $\times$  (C) is in close agreement with previously accepted values, and its significance in the five steels examined is discussed. Rolled sections of ingots, taken from the middle of the ingot position, were examined for their carbon and oxygen contents, determined in mid-rim and mid-core positions. A study is presented of the variations in these two elements in relation to the balanced composition as modified by the presence of manganese and the effect of pressure.

The results of the further examination of an ingot of rimming steel previously reported upon by Binnie (*Journal of The Iron and Steel Institute*, 1942, No. II., p. 283 p) are given in an Appendix. The oxygen and carbon values obtained in rim and core positions of top, middle and bottom sections provide additional interesting data on ingot position relative to the balanced composition.

## INTRODUCTION.

In three previous papers<sup>(1, 2, 3)</sup> one of the authors has recorded examinations of rimming-steel sections from the viewpoint of variations in composition from outside to centre, and perusal of the many Reports of the Committee on the Heterogeneity of Steel Ingots shows

\* Received October 12, 1943. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed in it are the authors', and are not necessarily endorsed by the Committee as a body.

the wide interest taken in the subject of effervescing steel. As a result of this work and that of many other investigators, notably Binnie,<sup>(4)</sup> Mitchell<sup>(5)</sup> and Hayes and Chipman,<sup>(6)</sup> it may be stated that the changes in composition, as affecting the common constituents, occurring as a result of the rimming action are now clearly understood. The theoretical aspect of the matter has been the subject of much controversy, particularly since the publication by Hultgren and Phragmén<sup>(7)</sup> of their excellent paper. Detailed comment on this paper has been made by Edwards<sup>(8)</sup> and by Myers.<sup>(9)</sup> Hultgren and Phragmén<sup>(7)</sup> may be said to have placed the study of rimming steel on a quantitative basis. In addition to a study of the many aspects of the rimming action, they postulate the ability to predict from the knowledge of its carbon content the progressive changes in composition expected to arise from the freezing of rimming steel. Hultgren and Phragmén's hypothesis is directed towards the changes in the *liquid* metal, and they suggest that at a given concentration of carbon and oxygen—termed the "balanced" composition—both elements will remain constant in the liquid metal during the progressive freezing of the rim zone so long as gas is being freely evolved. For higher carbon contents than the balanced composition, carbon will increase and oxygen decrease progressively in the liquid metal, while the converse will hold for metal of carbon content lower than the balanced composition. The latter, in the view of Hultgren and Phragmén, is probably not far removed from carbon 0·06%, oxygen 0·04%, and certain confirmation of these figures is found in the earlier work of one of the present authors. Two sections of rimming steel, one with a pit sample analysis of carbon 0·10%, manganese 0·31%, showed rim-zone variations expected of metal above the balanced composition, while the other, containing carbon 0·047%, manganese 0·10%, varied in the manner expected of rimming steel slightly below the balanced composition. Binnie<sup>(4)</sup> calculated the effects of manganese and of pressure on the balanced composition and indicated that both operate in the direction of increasing the required carbon content. Typical examples by Binnie are :

- (1) Manganese nil.
- At 1 atm. pressure, carbon 0·045%.
- At 2 atm. pressure, carbon 0·063%.
- (2) Manganese 0·30%.
- At 1 atm. pressure, carbon 0·063%.
- At 2 atm. pressure, carbon 0·09%.

In this paper Binnie reported a detailed examination of an ingot from a cast, the pit sample of which was reported to contain carbon 0·08%, manganese 0·30%. The excellent calculations in the paper would lead one to expect that the top portion of this ingot would be *above* the balanced composition, but the analyses of the ingot, reported by Binnie, indicate very definitely that the steel was *below* the balanced composition.

Dr. Binnie very kindly provided the present authors with sections of this ingot for further examination, and the results are contained in an Appendix hereto.

Mitchell<sup>(5)</sup> describes the features of three ingots made at Denain and four ingots of different sizes from the same basic Bessemer cast at Corby. Although the pit samples of the Denain ingots contain 0·06% of carbon or less, the average core carbons of two ingots are greater than the pit sample, while in the third ingot the pit-sample carbon (0·047%) is very slightly greater than the average core figure (0·045%), indicating that the first two samples are above the balanced composition and the third is probably below. Also, in the Corby ingots the mid-core carbon exceeds the pit-sample carbon of 0·055% (manganese 0·49%), again indicating steel above the balanced composition. In discussion of these results, Dickie<sup>(10)</sup> emphasises that all Mitchell's ingots are above the balanced composition and suggests that the carbon content of the latter should be placed at about 0·04%. Moreover, Dickie suggests that manganese does not have the marked effect ascribed to it by Binnie. Both Kerlie<sup>(11)</sup> and Binnie,<sup>(12)</sup> in discussion, show the importance of pressure in the rimming action, and the many examples now before the Ingot Committee illustrate fully this effect. It will be found that, in general, the carbon content in the rim zone is highest at the bottom of the ingot and in the core zone is highest at the top. Thus, the maximum difference in average rim and core carbon contents occurs in the top portion of the ingot, where the pressure is of the order of one atmosphere. Towards the bottom the difference is less, owing, it is suggested, to the greater pressure (2 atm. or more) exerted there. Consequently, while Binnie is probably correct in his assertion that there is no single balanced composition covering all rimming steels, it perhaps is more important to state that a *single balanced composition does not exist for all parts of the same ingot.*

#### PRESENT INVESTIGATION.

It should be noted that all the work yet carried out on the Hultgren and Phragmén hypothesis has been done by the indirect method of approach. Solid steels have been examined, in their different zones, after freezing, whereas the Hultgren and Phragmén course of the changes refers to the liquid metal. The present work has also employed the indirect method and consists of the examination of five casts of rimming steel, of pit-sample carbon contents between 0·04% and 0·14%, the objective being to correlate pit-sample carbon and oxygen contents with rim and core carbon and oxygen contents in relation to the balanced composition. The evidence presented is of a limited nature, but it does serve to throw more light on the theory and practice of rimming and gives useful data on the correlation of carbon and oxygen in rimming steel.

*Sampling Procedure.*

Five typical rimming-steel casts were sampled in the Templeborough Melting Shop of The United Steel Companies, Ltd., by a modified "bomb" technique.<sup>(13)</sup> The samples were taken in the usual pit-sample test mould, filled with a crumpled mass of 30-gauge aluminium wire (weighing 10 g.), from the stream of liquid metal leaving the ladle nozzle. Sound and reasonably homogeneous samples were obtained, and it was considered that the state of equilibrium between the carbon and oxygen presumed to exist in the ladle metal would be preserved in samples taken in this manner. Three such samples were taken from each cast representing the beginning, middle and end of the ingot-casting period. Details of the charges and cast histories of these five heats are given in Tables I and II.

TABLE I.—*Basic Open-Hearth Rimming Steel, Cast No. 31/979, made Mar. 13, 1943. Furnace Details.*

Charge.	Composition.				Weight.				
	Mn. %.	Si. %.	S. %.	P. %.	Tons.	Cwt.	Tons.	Owt.	
Basic iron . . .	1.0	0.8	0.07	1.5	12	17	23	2	
Indian iron . . .	1.25	1.1	0.05	0.3	10	5			
Scrap . . .	0.6	0.15	0.05	0.05	63	13	63	13	
Lime . . .	...	...	...	...	1	6			
Limestone . . .	...	...	...	...	3	2	4	15	
Fluorspar . . .	...	...	...	...	7				
							Total	91 10	
Analysis.									
Details of Heat.	C. %.	Mn. %.	S. %.	P. %.	Fe in Slag. %.	SiO <sub>2</sub> in Slag. %.	Time.	Furnace Time.	Tamp. °C.
Commenced charging . . .	...	...	...	...	...	...		Hr. Min.	
Finished charging . . .	...	...	...	...	...	...	23.35	...	...
Clear melted . . .	0.55	...	...	...	6.5	15.5	05.40	6 5	...
1st bath sample . . .	...	...	...	...	...	...	08.55	9 20	...
Lime added, 40 cwt.	...	...	...	...	...	...	...	...	...
Spar added, 7 cwt.	...	...	...	...	...	...	...	...	...
Mill scale added, 25 cwt.	...	...	...	...	...	...	...	...	...
Ore added, 30 cwt.	...	...	...	...	...	...	...	...	...
2nd bath sample . . .	0.35	...	...	...	15.0	...	10.10	10 35	...
3rd . . .	0.12	...	...	...	...	...	10.35	11 00	...
4th . . .	0.12	0.13	0.031	0.025	...	...	10.50	11 15	1585
5th . . .	0.05	...	...	...	23.7	...	11.10	11 35	1605
Tapped . . .	...	...	...	...	...	...	11.20	11 45	...
Ladle additions : Aluminium, 55 lb.									
Mould additions : 1½ oz. of aluminium per ton added just before plating.									
Method of teeming : Direct, cooler-plated.									
Cast analyses :									
1st pit sample . . .	0.04	0.10	...	...	...	...	...	...	...
2nd . . .	0.04	0.10	0.034	0.018	...	...	...	...	...
3rd . . .	0.04	0.10	0.036	0.019	...	...	...	...	...

I., II., III., IV. and V. The low-carbon cast was poured direct, the other four casts being poured uphill.

TABLE II.—*Basic Open-Hearth Rimming Steel, Cast No. 29/9106 made Nov. 4, 1942. Furnace Details.*

Charge.	Composition.				Weight.				
	Mn. %.	Si. %.	S. %.	P. %.	Tons.	Cwt.	Tons.	Cwt.	
Basic iron . . .	1.0	0.8	0.07	1.5	22	2	22	2	
Scrap . . .	0.6	0.15	0.05	0.05	61	11	61	11	
Lime . . .	...	...	...	...	3	3	3	16	
Fluorspar . . .	...	...	...	...	13	3			
							Total	87 9	
Details of Heat.	Analysis.						Time.	Furnace Time.	Temp. °O.
	C. %.	Mn. %.	S. %.	P. %.	Fe in Slag. %.	SiO <sub>2</sub> in Slag. %.			
Commenced charging . . .	...	...	...	...	...	...	00.10	...	...
Finished charging . . .	...	...	...	...	...	...	06.00	5 50	...
Clear melted . . .	...	...	...	...	...	...	09.47	9 37	...
1st bath sample . . .	0.37	...	...	...	5.5	18.2	...	...	...
Lime added, 41 cwt.	...	...	...	...	...	...	09.50	9 40	...
Spas added, 11 cwt.	...	...	...	...	...	...	10.10	10 00	...
Scale added, 30 cwt.	...	...	...	...	...	...	10.20	10 10	...
2nd bath sample . . .	0.12	...	...	...	13.5	...	11.30	11 20	...
Immersion temp. . .	...	...	...	...	...	...	11.45	11 35	1613
3rd bath sample . . .	0.14	0.14	0.044	0.025	...	...	12.00	11 50	...
4th . . .	0.11	...	...	...	...	...	12.05	11 55	...
5th . . .	0.09	...	...	...	...	...	12.16	12 06	...
6th . . .	0.07	...	...	...	...	...	12.27	12 17	...
Immersion temp. . .	...	...	...	...	...	...	12.30	12 20	1614
Tapped . . .	...	...	...	...	...	...	12.35	12 25	...
Tapping slag . . .	...	...	...	...	16.5	...	...	...	...
Ladle additions : Ferro-manganese, 7 cwt.; aluminium, 20 lb.									
Mould additions : None.									
Method of teeming : Cast uphill.									
Cast analyses :									
Pit sample . . .	0.07	0.34	0.041	0.018	...	...	...	...	...

Four of the casts were processed to slab and one to 2-in. square billet. Samples from the middle of an ingot from each of the three plates corresponding to the pit samples were obtained.

#### Chemical Analysis.

Oxygen (by the vacuum fusion method) and carbon determinations were made on all the pit samples, with results as given in Table VI. Oxygen and carbon were also examined on the slab and billet samples at two positions :

- (a) Midway between the edge and the rim-core junction;
- (b) Midway between the rim-core junction and the centre.

The results obtained are shown in Table VII.

TABLE III.—*Basic Open-Hearth Rimming Steel, Cast No. 27/6293, made Dec. 9, 1942. Furnace Details.*

Charge.	Composition.				Weight.			
	Mn. %.	Si. %.	S. %.	P. %.	Tons.	Cwt.	Tons.	Cwt.
Basic iron . . .	1.0	0.8	0.07	1.5	22	11	22	11
Scrap . . .	0.6	0.15	0.05	0.05	62	4	62	4
Lime . . .	...	...	...	...	3	8	3	13
Fluorspar . . .	...	...	...	...	5	8	3	13
							Total	88 8

Details of Heat.	Analysis.						Time.	Furnace Time.	Temp. °C.
	C. %.	Mn. %.	S. %.	P. %.	Fe in Slag. %.	SiO <sub>2</sub> in Slag. %.			
Commenced charging . . .	...	...	...	...	...	...	06.20	...	...
Finished charging . . .	...	...	...	...	...	...	11.50	5 30	...
Clear melted . . .	...	...	...	...	...	...	15.50	9 30	...
1st bath sample . . .	0.46	...	...	...	5.5	19.0	...	...	...
Lime added, 53 cwt.	...	...	...	...	...	...	15.50	9 30	...
Spar added, 7 cwt.	...	...	...	...	...	...	...	...	...
Ore added, 40 cwt.	...	...	...	...	...	...	16.05	9 45	...
Scale added, 10 cwt.	...	...	...	...	...	...	16.10	9 50	...
2nd bath sample . . .	0.24	...	...	...	17.9	...	16.40	10 20	...
3rd " . . .	0.19	...	...	...	...	...	17.00	10 40	...
Immersion temp. . .	...	...	...	...	...	...	17.20	11 00	1603
4th bath sample . . .	0.17	0.13	0.037	0.025	...	...	17.20	11 00	...
5th " . . .	0.07	...	...	...	...	...	17.32	11 12	...
Tapped " . . .	...	...	...	...	...	...	18.00	11 40	...
Tapping slag . . .	...	...	...	...	19.0	...	...	...	...
Ladle additions : Ferro-manganese, 7 cwt.; aluminium, 20 lb.									
Mould additions : None.									
Method of teeming : Cast uphill.									
Cast analyses :									
1st pit sample . . .	0.075	0.30	...	...	...	...	...	...	...
2nd " . . .	0.075	0.30	0.031	0.015	...	...	...	...	...
4th " . . .	0.075	0.28	0.031	0.017	...	...	...	...	...

### Metallurgical Examination.

The full cross-section of the small billet and small slab was sulphur-printed. On account of the large flat section of the other three slab samples, the half cross-section was examined by sulphur-printing, with the following observations :

- *Cast 31/979* : 2-in. square billet section. Junction between rim and core clearly marked.

- Cast 29/9106* : Evidence of double rim. Junction between rim and core not clearly defined.

- Cast 27/6293* : No evidence of double rim. Rim-core junction clearly marked.

- Cast 30/4918* : No evidence of double rim. Rim-core junction less marked than in cast 27/6293.

SULPHUR PRINTS OF BASIC OPEN-HEARTH RIMMING STEELS.

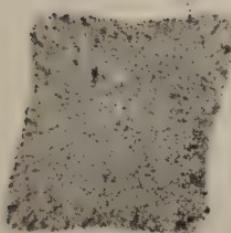


FIG. 1.—Billet Section from Cast 31/979.



FIG. 2.—Slab Sections from Cast 29/9106.



FIG. 3.—Slab Sections from Cast 27/6293.

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SULPHUR PRINTS OF BASIC OPEN-HEARTH RIMMING STEELS.



FIG. 4.—Slab Sections from Cast 30/4918.



FIG. 5.—Slab Sections from Cast 35/7407.

[*Swinden, Stevenson & Speight.*

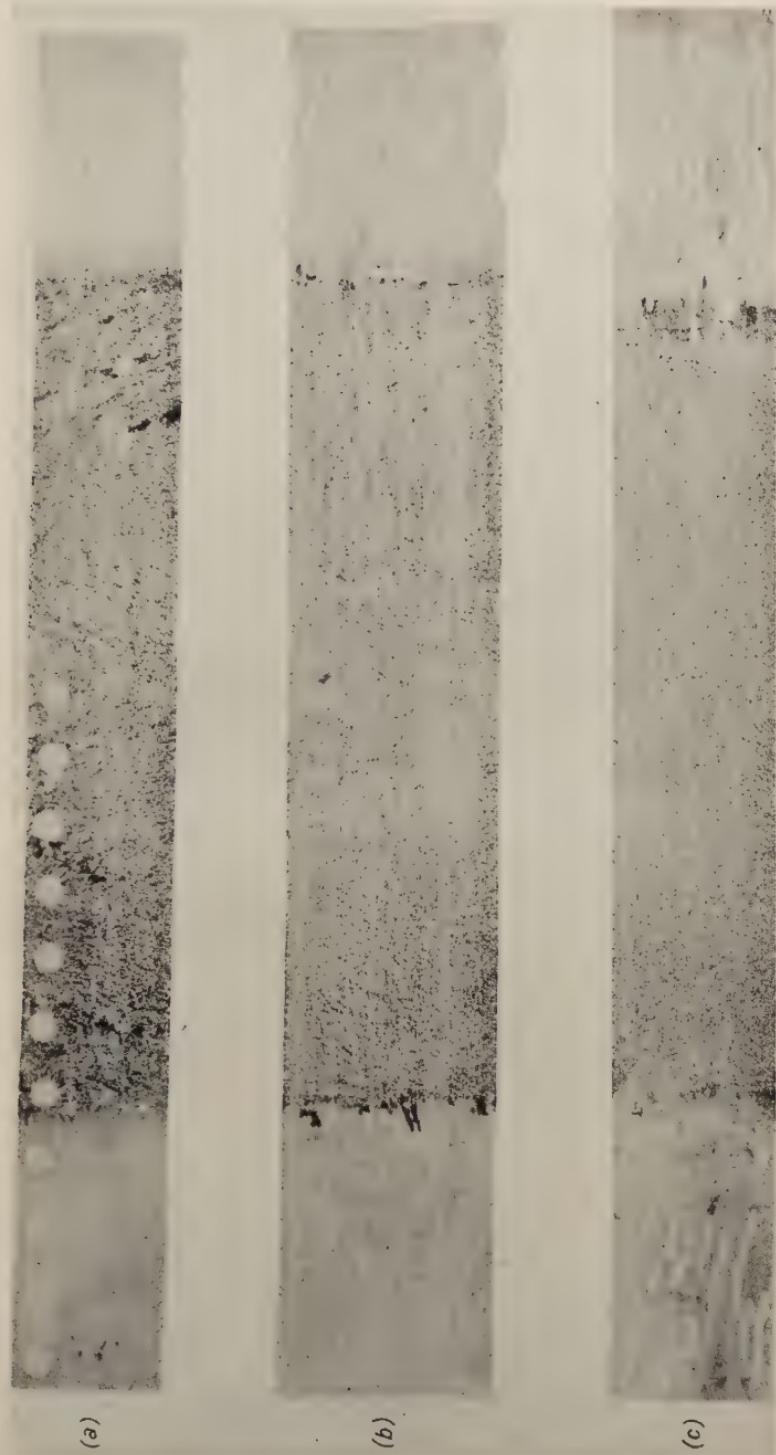


FIG. 6.—Rimming Steel (Binnic<sup>(7)</sup>). Sulphur prints of (a) top, (b) middle and (c) bottom sections of the ingot.



*Cast 35/7407*: No evidence of double rim. Rim-core junction slightly less marked than in cast 30/4918.

Photographs of the sulphur prints are shown in Figs. 1 to 5.

The sulphur prints reveal certain differences in the proportion of rim to core; consequently, this ratio has been calculated and is given, together with an abstract of the carbon and oxygen data, in Table VIII.

TABLE IV.—*Basic Open-Hearth Rimming Steel, Cast No. 30/4918, made Nov. 11, 1942. Furnace Details.*

Charge.	Composition.				Weight.			
	Mn. %.	Si. %.	S. %.	P. %.	Tons.	Cwt.	Tons.	Cwt.
Basic iron . . .	1.0	0.8	0.07	1.5	13	3		
Indian iron . . .	1.25	1.1	0.05	0.3	7	3	20	6
Scrap . . .	0.6	0.15	0.05	0.05	6 $\frac{1}{4}$	7	64	7
Lime . . .	...	...	...	...	3	5		
Fluorspar . . .	...	...	...	...	5	3	10	
					Total	88		3

Details of Heat.	Analysis.						Time.	Furnace Time.	Temp. °C.
	C. %.	Mn. %.	S. %.	P. %.	Fe in Slag. %.	SiO <sub>2</sub> in Slag. %.			
Commenced charging . . .	...	...	...	...	...	...	22.45	...	...
Finished charging . . .	...	...	...	...	...	...	04.00	5 15	...
Clear melted . . .	...	...	...	...	...	...	10.30	11 45	...
1st bath sample . . .	0.17	...	...	...	6.0	12.5	...	...	...
Lime added, 25 cwt.	...	...	...	...	...	...	10.35	11 50	...
Spar added, 10 cwt.	...	...	...	...	...	...	...	...	...
2nd bath sample . . .	0.13	0.17	0.037	0.010	15.0	...	11.25	12 40	...
Immersion temp. . .	...	...	...	...	...	...	11.35	12 50	1605
3rd bath sample . . .	0.11	...	...	...	...	...	11.42	12 57	...
Tapped . . .	...	...	...	...	...	...	11.50	13 05	...
Tapping slag . . .	...	...	...	...	17.0	11.0	...	...	...
Ladle additions : Ferro-manganese, 9 cwt.; anthracite coal, 72 lb.; aluminium, 3 lb.									
Mould additions : None.									
Method of teeming : Cast uphill.									
Cast analyses :									
Pit sample . . .	0.12	0.52	0.035	0.022	...	...	...	...	...

#### *Observations on the Results Obtained.*

(1) Only in the casts of low carbon content was an addition of aluminium made to the ladle. The amount of aluminium so added is a maximum with the lowest carbon content and decreases as the pit carbon increases, as shown in Table IX.

(2) The oxygen contents of the pit samples vary inversely with their carbon contents and the product of these two concentrations ( $O$ )  $\times$  ( $C$ ) for the liquid metal ranges between 0.00200 and 0.00255,

TABLE V.—*Basic Open-Hearth Rimming Steel, Cast No. 35/7407, made Dec. 18, 1942. Furnace Details.*

Charge.	Composition.				Weight.				
	Mn. %.	Si. %.	S. %.	P. %.					
Basic iron . .	1.0	0.8	0.07	1.5	15	10	21	11	
Cast metal . .	0.75	2.0	0.09	0.6	6	1	62	11	
Scrap . .	0.6	0.15	0.05	0.05	62	11	62	11	
Lime . .	...	...	...	...	3	8	3	13	
Fluorspar . .	...	...	...	...	5				
					Total	87		15	
Details of Heat.	Analysis.						Time.	Furnace Time.	Temp. ° C.
	C. %.	Mn. %.	S. %.	P. %.	Fe in Slag. %.	SiO <sub>2</sub> in Slag. %.			
Commenced charging .	...	...	...	...	...	...	03.35		
Finished charging .	...	...	...	...	...	...	08.35	5	0
Clear melted .	...	...	...	...	...	...	11.30	7	55
1st bath sample .	0.46	...	...	...	2.0	15.8	...	...	...
Lime added, 24 cwt.	...	...	...	...	...	...	11.30	...	...
Spar added, 7 cwt.	...	...	...	...	...	...	...	...	...
2nd bath sample .	0.44	...	...	...	...	...	11.45	8	10
Mill scale added, 30 cwt. .	...	...	...	...	...	...	11.55	8	20
3rd bath sample .	0.36	...	...	...	10.5	...	12.20	8	45
4th .	0.20	...	...	...	...	...	12.35	9	00
5th "	0.16	0.18	0.038	0.025	...	...	12.45	9	10
Immersion temp. .	...	...	...	...	...	...	12.50	9	15
6th bath sample .	0.11	...	...	...	...	...	13.00	9	25
Tapped .	...	...	...	...	...	...	13.05	9	30
Ladle additions : Ferro-manganese, 4½ cwt.; anthracite coal, 144 lb.									
Method of teeming : Cast uphill.									
Mould additions : 1½ oz. of aluminium per ton of steel.									
Cast analyses :									
1st pit sample .	0.13	0.30	...	...	...	...	...	...	...
2nd .	0.14	0.29	0.039	0.025	...	...	...	...	...
3rd .	0.14	0.28	0.040	0.027	...	...	...	...	...

the mean result being 0.00225. This value agrees fairly well with that due to Vacher and Hamilton,<sup>(14)</sup> whose equilibrium constant of 0.00247 is generally accepted.

(3) Herty,<sup>(15)</sup> Schenck<sup>(16)</sup> and Schenck, Riess and Brüggemann<sup>(17)</sup> have determined the value (FeO) × (C) for both acid and basic furnaces by a method similar to the present procedure, and Schenck<sup>(16)</sup> in particular suggested that the equilibrium constant increased with increasing carbon content. A similar slight tendency may be deduced from the present experiments, although the authors would not accept entirely the explanation suggested by Schenck, i.e., the presence of a dissociated polymerised carbide. It should be stated, however, that Schenck's work dealt substantially with steels of higher carbon contents than those at present under discussion.

If it be postulated that the metal in the furnace at the end of the

TABLE VI.—*Basic Open-Hearth Rimming Steel Casts. Carbon and Oxygen Determinations on Pit Samples.*

Cast No.	Bath Temp. before Tapping. °C.	Ladle Additions.	Mould Additions.	Oxygen (by Vacuum Fusion). %.	Car-bon. %.	Product (O) × (O).
31/979	1605	55 lb. aluminium.	1½ oz. of (1) aluminium (2) per ton. (3)	0.055 0.049 0.045	0.04 0.04 0.04	0.00220 0.00196 0.00180 } 0.00200
29/9106	1614	7 cwt. ferro-manganese. 20 lb. aluminium.	No addition. (1) (2) (4)	0.0325 0.0285 0.0325	0.065 0.07 0.07	0.00211 0.00200 0.00227 } 0.00215
27/6293	1603	7 cwt.-ferro-manganese. 20 lb. aluminium.	No addition. (1) (2) (4)	0.033 0.031 0.0305	0.075 0.075 0.075	0.00247 0.00232 0.00229 } 0.00235
30/4918	1605	9 cwt. ferro-manganese. 3 lb. aluminium. 72 lb. anthracite.	No addition. (1) (2) (3)	0.0175 0.018 0.018	0.115 0.12 0.115	0.00202 0.00216 0.00207 } 0.00210
35/7407	1616	4½ cwt. ferro-manganese. 144 lb. anthracite.	1½ oz. of (1) aluminium (2) per ton. (3)	0.0175 0.018 0.020	0.13 0.14 0.14	0.00228 0.00252 0.00280 } 0.00255

TABLE VII.—*Basic Open-Hearth Rimming Steel Casts. Carbon and Oxygen Determinations on Billet and Slab Samples.*

Cast No.	Carbon of Pit Sample. %.	Billet and Slab Samples.			
		Position of Sample.	Oxygen. %.	Carbon. %.	Product (O) × (O).
Cast 31/979; 2-in. square bil- let.	(1)	Rim	0.022 <sub>5</sub>	0.015	0.00034
	(2)	...	...	...	...
	(3)	Mid-core	0.045 <sub>5</sub>	0.040	0.00182
Cast 29/9106; 5 in. × 1½-in. slab.	(1)	(a) Mid-rim (b) Mid-core	...	0.035 0.05	...
	(2)	(a) Mid-rim (b) Mid-core	0.015 0.028	0.035 0.065	0.00053 0.00182
	(4)	(a) Mid-rim (b) Mid-core	...	0.03 0.07	...
Cast 27/6293; 15 in. × 1½-in. slab.	(1)	(a) Mid-rim (b) Mid-core	...	0.045 0.11	...
	(2)	(a) Mid-rim (b) Mid-core	0.012 0.014	0.04 0.10	0.00048 0.00140
	(4)	(a) Mid-rim (b) Mid-core	...	0.045 0.10	...
Cast 30/4918; 14½ in. × 1½-in. slab.	(1)	(a) Mid-rim (b) Mid-core	...	0.08 0.115	...
	(2)	(a) Mid-rim (b) Mid-core	0.010 0.011	0.07 0.16	0.00070 0.00176
	(3)	(a) Mid-rim (b) Mid-core	...	0.07 0.15	...
Cast 35/7407; 14½ in. × 1½-in. slab.	(1)	(a) Mid-rim (b) Mid-core	...	0.08 0.14	...
	(2)	(a) Mid-rim (b) Mid-core	0.010 0.012	0.075 0.14	0.00075 0.00168
	(4)	(a) Mid-rim (b) Mid-core	...	0.065 0.14	...

TABLE VIII.—*Basic Open-Hearth Rimming Steel Casts. Ratio of Rim-Zone Area to Core-Zone Area shown in the Sulphur Prints of Billet and Slab Cross-Sections.*

Sample No.	Pit Sample.		Slab Sample.		Rim-Core Ratio.
	Carbon, %.	(O) × (C).	Carbon, %.	(O) × (C).	
Cast 31/979; 2-in. square billet.	0.04	0.00220	(a) Rim 0.015 (b) Core 0.04	0.00034 0.00182	1.91 { 1.91
	0.04	0.00196			
	0.04	0.00180			
Cast 29/9106; 5 in. × 1½-in. slab.	0.065	0.00211	(a) Rim 0.035 (b) Core 0.065	0.00053 0.00182	1.53 { 1.53
	0.07	0.00200			
	0.07	0.00227			
Cast 27/6293; 15 in. × 1½-in. slab.	0.075	0.00247	(a) Rim 0.04 (b) Core 0.10	0.00048 0.00140	2.31 { 2.04
	0.075	0.00232			
	0.075	0.00229			
Cast 40/4918; 14½ in. × 1½-in. slab.	0.115	0.00202	(a) Rim 0.07 (b) Core 0.16	0.00070 0.00176	1.53 { 1.51
	0.12	0.00216			
	0.115	0.00207			
Cast 35/7407; 14½ in. × 1½-in. slab.	0.13	0.00228	(a) Rim 0.075 (b) Core 0.14	0.00075 0.00168	1.12 { 1.10
	0.14	0.00252			
	0.14	0.00280			

TABLE IX.—*Basic Open-Hearth Rimming Steel Casts. Summary of Pit-Sample Analyses and Ladle and Mould Additions.*

Cast No.	Pit-Sample Analysis.		Aluminium and Anthracite Additions.	
	Carbon, %.	Manganese, %.	Ladle.	Mould.
31/979	0.04	0.10	55 lb. aluminium	1½ oz. aluminium per ton just before plating.
29/9106	0.07	0.34	20 lb. aluminium	No addition.
27/6293	0.075	0.30	20 lb. aluminium	No addition.
30/4918	0.115	0.52	3 lb. aluminium	No addition.
35/7407	0.135	0.29	72 lb. anthracite	1½ oz. aluminium per ton.

refining period more closely approaches equilibrium conditions than at any other stage, then the equilibrium constant  $(O) \times (C)$  should be achieved in all cases in the absence of association or dissociation. The product will, however, be affected by the subsequent treatment of the metal in the ladle, in one of two directions, by :

- (a) Aluminium treatment;
- (b) Carbon addition.

The effect of an aluminium addition is to remove part of the oxygen content from the sphere of reaction, and, on subsequent flotation of alumina particles, the residual oxygen content will

be less than that required for saturation. Consequently, the product  $(O) \times (C)$  will be lower than the equilibrium constant for that particular temperature.

The effect of the addition of carbon to metal in equilibrium with respect to carbon and oxygen increases the concentration of one of the reactants. Hence, to maintain the equilibrium, the oxygen content must be reduced. However, it is doubtful whether sufficient reaction occurs in the ladle to readjust the equilibrium to the new conditions, and the product  $(O) \times (C)$  will thus probably exceed the true equilibrium value.

The results given in Table VI. illustrate the above effects. Cast 31/979, of low carbon content, shows the lowest average value of  $(O) \times (C)$  (0.00200) coincident with the largest aluminium addition to the ladle. On the other hand, cast 35/7407, with the highest carbon content, has the highest  $(O) \times (C)$  value (0.0025<sub>5</sub>), and this cast was treated with anthracite.

(4) The data presented in Tables VII. and VIII., dealing with the composition and extent of the rim and core of the samples, suggest the following comments :

(a) In all five casts the rim carbon is less than the pit-sample carbon content; in three cases, casts 31/979, 29/9106 and 35/7407, the carbon content of the core approximates to the pit-sample carbon whilst in the remaining two, 27/6293 and 30/4918, the core carbon is greater than the pit sample. This would indicate that in those steels where the core carbon is equal to the carbon content of the pit sample, a greater loss of carbon monoxide occurred during the solidification of the ingots. Approximate calculation of the mean carbon of the sample, based on the distribution in the rim and core, confirms a greater loss of carbon monoxide in the solidification of these three casts.

The actual loss of carbon (taking the mid-rim and mid-core analyses as the average of the entire rim and core, respectively) is shown in Table X. These results should be regarded as only approximate, as the calculations were made on an area (not volume) basis \* and the mid-rim carbon figure is indicative, rather than a definite measure, of the average carbon value across the rim zone.

Loss of carbon monoxide in solidification is illustrated graphically in Fig. 7, in which carbon and oxygen contents of (a) pit samples, (b) mid-core samples and (c) mid-rim samples are shown. Furthermore, all the three curves are of hyperbolic form, indicating that, irrespective of the ladle carbon content of rimming steel in the range 0.04–0.14%, the relative contents of carbon and oxygen present are governed by the  $\text{FeO} + \text{C}$  reaction.

\* This was necessary as only slices were examined and it was impossible to calculate on a volume basis without having a vertical section of the ingot.

TABLE X.—Calculated Carbon Loss during Solidification (Approximate).

Cast No.	Carbon in Pit Sample. %.	Calculated Average Carbon in Section. %.	Carbon Loss. %.
31/979	0.04	0.0235	0.0165
29/9106	0.07	0.048	0.022
27/6293	0.075	0.061	0.014
30/4918	0.12	0.106	0.014
35/7407	0.14	0.106	0.024

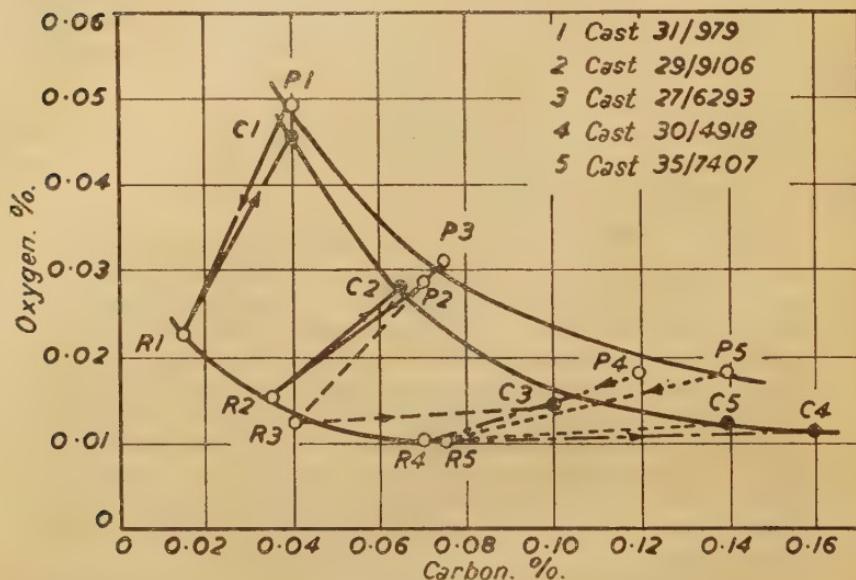


FIG. 7.—Carbon and Oxygen Relationship in (a) pit, (b) mid-core and (c) mid-rim samples from basic open-hearth rimming-steel casts.

(b) The product ( $O \times C$ ) has been calculated for the solid samples. As expected, a lower value is found in the rim, where solidification occurs under conditions of free gasification and normal pressure. A higher value is found in the core, where gasification is restricted by the external pressure of the solidifying metal. The ratio between this value for the core and the rim is very striking; thus :

$$\frac{(O \times C) \text{ for core}}{(O \times C) \text{ for rim}}$$

is slightly greater than 5 for the cast of lowest carbon content, and the ratio decreases with increasing carbon content to approximately 2 in the rimming steel of highest carbon content. The value of the product ( $O \times C$ ) for the core zone is almost

constant for all the five casts examined, being of the order of 0.0017.

(c) The rim-core ratio as calculated from the cross-section of the samples is also interesting. As shown in Table VIII., the highest-carbon cast has a markedly smaller proportion of rim, while the low-carbon casts have larger proportions of rim to core.

Reverting to the question of the balanced composition, it is at once evident from the direction of the lines  $P3R3C3$ ,  $P4R4C4$  and  $P5R5C5$  in Fig. 7 that these three casts, 27/6293, 30/4918 and 35/7407, respectively, are above the balanced composition. The position regarding casts 31/979 and 29/9106 is, however, quite different. The number of samples available—one pit sample, one mid-rim sample and one mid-core sample—is insufficient to give a definite pronouncement. It would appear, however, from the indications given by the lines  $P1R1C1$  and  $P2R2C2$  that these two steels are very near to the balanced composition, since the angles subtended are almost zero. This would suggest the occurrence of a balanced composition :

- (a) at approximately 0.04% carbon, 0.10% manganese, and
- (b) at approximately 0.07% carbon, 0.34% manganese.

The effect of manganese on the required carbon for the balanced composition is thus strikingly demonstrated, and it is interesting to compare these values with those calculated by Binnie.<sup>(4)</sup> A selection of these is quoted earlier. At  $1\frac{1}{2}$  atm. pressure and nil manganese, interpolation of Binnie's values shows a balanced-composition carbon content of the order of 0.055%; at the same pressure and 0.30% manganese the carbon figure is raised to approximately 0.075%.

The inference from these results is that the lowest-carbon cast examined in the present paper (No. 31/979), whilst very close to the balanced composition, should actually be below it. In this connection, it should be pointed out that all analytical results are reported in the paper to the normal limits of accuracy obtainable in the laboratories of the authors, *i.e.*, in carbon, to 0.005%, and in oxygen to 0.0005%; the curves in Fig. 7 have been drawn on this basis. It is immediately apparent, however, that only slight variations in the carbon contents of the pit and core samples for cast 31/979 would alter materially the form of the curve for this example; in view of the critical considerations involved, further determinations of carbon content in these two samples have in fact been made with extreme care and accuracy. The mean of seven such determinations gives the following results on the samples from cast 31/979 :

Pit sample . . . . .	0.042%	of carbon.
Mid-rim sample . . . . .	0.016%	"
Mid-core sample . . . . .	0.038%	"

Although the differences revealed by these further determinations are only slight as compared with the normal results of 0.04% for

both the pit sample and the mid-core sample, they are sufficient to indicate that this cast is probably *just below* the balanced composition for the manganese content in question (0·10%) and the position in the ingot from which the samples were taken.

The authors are of the opinion that Binnie's calculations regarding the balanced composition and the influence of manganese on it are substantially correct. Most commercial rimming steels are above the balanced composition (and in this respect, cast 31/979 is of unusual type), except in those parts of the ingot where the metal is under the influence of a high ferrostatic head. The influence of ferrostatic pressure must be taken into account, and the authors reaffirm the necessity for locating the position of the sample relative to the ingot in interpreting data concerning the balanced composition.

The authors are pleased to record their appreciation of the assistance rendered in this investigation by the Metallurgical Department and the Templeborough Melting Shop staff of Messrs. Steel, Peech and Tozer. Also, their thanks are due to the Directors of The United Steel Companies, Ltd., for the necessary permission for publication.

*APPENDIX.—Examination at Stocksbridge of Sections from an Ingot of Basic Open-Hearth Rimmed Steel previously Reported upon by Dr. D. Binnie.*

In paper No. 13/1942 of the Committee on the Heterogeneity of Steel Ingots, Dr. Binnie reported the results of his examination of "An Ingot of Rimmed Steel Made by the Basic Open Hearth Process."<sup>(4)</sup> Relevant details of the ingot are as follows :

*Pit-Sample Analysis :*

Carbon. %.	Manganese. %.	Sulphur. %.	Phosphorus. %.
0·08	0·29	0·042	0·018

*Ingot Weight :* 3 tons.

*Cast :* Direct.

*Dimensions (approx.) :* 68 in. in length

22 in. at the bottom, tapering to 19½ in. at the top.

Transverse sections were cut at positions respectively a quarter, a half and three-quarters of the height from a half ingot sectioned longitudinally. These sections thus represent the bottom, middle and top of the ingot, and the sulphur prints of the faces corresponding to the central axis of the ingot are shown in Fig. 6.

At the positions indicated in Fig. 8, pieces  $\frac{1}{2}$  in. in width were taken from the slices for the determination of total oxygen by vacuum fusion and of carbon. The positions indicated in Fig. 8 may be designated :

- (a) The extreme edge of the rim,
- (b) mid rim,

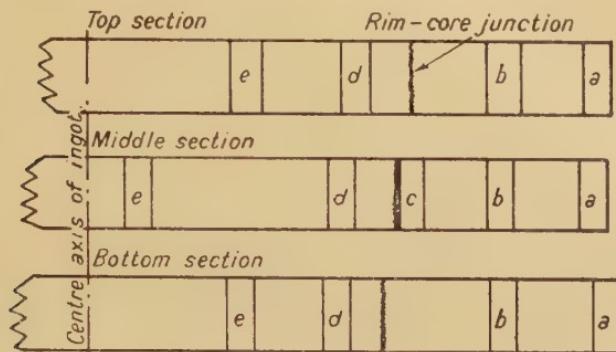


FIG. 8.—Rimming Steel (Binnie<sup>(4)</sup>). Position of samples for carbon and oxygen determinations.

- (c) in the rim near to the rim-core junction,
- (d) 1 in. inside the core, and
- (e) well inside the core.

The results obtained are given in Table XI.

TABLE XI.—Rimming Steel (Binnie<sup>(4)</sup>). Carbon and Oxygen Contents at Positions corresponding to Top, Middle and Bottom of Ingot Section.

Position.	Outer Edge of Rim. (a)	Mid Rim. (b)	In Rim near Rim-Core Junction. (c)	1-in. Inside Core. (d)	Midway between Junction and Centre. (e)
Top section :					
Carbon. % .	0.045	0.025	...	0.050	0.045
Oxygen. % .	0.032	0.016 <sub>5</sub>	...	0.058	0.041
Middle section :					
Carbon. % .	0.040	0.025	0.035	0.045	0.040 *
Oxygen. % .	0.038	0.016	0.028	0.036	0.035
Bottom section :					
Carbon. % .	0.045	0.035	...	0.040	0.035
Oxygen. % .	0.043	0.023 <sub>5</sub>	...	0.032 <sub>5</sub>	0.032 <sub>5</sub> *

\* Nearer central axis of ingot.

The results are largely confirmatory of previous data on sections of rimming steel. It may be noted that :

- (1) Carbon at the extreme edge has the same value in all three bars.
- (2) The highest oxygen content at the extreme edge is found in the bottom bar.
- (3) The mid-rim positions have lower carbon contents than the extreme edge, with the widest difference in the top section.
- (4) Oxygen in the mid-rim position is lower than at the outside edge, but is again highest in the bottom section.

(5) Just inside the core, both carbon and oxygen are higher, carbon being as high as in the extreme edge of the rim.

(6) Oxygen inside the core is highest in the top section, which is 0·04% higher than the mid-rib position in the top section, the corresponding increase in the bottom section being only 0·009% of oxygen.

(7) Major segregation effects in respect to carbon and oxygen are found in the top section. This is in line with the segregation of the other elements in rimming steel.

This examination affords excellent confirmation of the differences obtained in carbon and oxygen contents at different parts of the same ingot of rimming steel. In fact, according to the values for the balanced composition suggested by Hultgren and Phragmén, on the basis of free gas evolution, the variations in the upper section are in line with a rimming steel below the balanced composition; the behaviour of the middle section is that of material having the balanced composition, whilst the data available do not permit of a definite opinion regarding the bottom section.

It is regretted that the pit sample is no longer available for further examination, as, in the light of the foregoing data, the authors would have anticipated that the pit-sample carbon content would have been nearer 0·05% than 0·08%.

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- (15) HERTY : *Metals and Alloys*, 1930, vol. 1, p. 883.
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- (17) SCHENCK, RIESS and BRÜGGEMANN : *Zeitschrift für Elektrochemie*, 1932, vol. 38, p. 562.

## CORRESPONDENCE.

Dr. H. A. DICKIE (Messrs. Stewarts and Lloyds, Ltd., Corby) wrote: It is not clear why the authors, after themselves noting that their evidence is of a "limited nature" and that the number of samples is "insufficient to give a definite pronouncement," should consider that the alleged effect of manganese on the balanced composition is "strikingly demonstrated" by their results. Their conclusion hinges on the results for cast 29/9106, which are, however, contradicted by the results (Fig. 7) for a similar cast 27/6293, and again by the results for a similar manganese, lower-carbon cast in their Appendix (Table XI.).

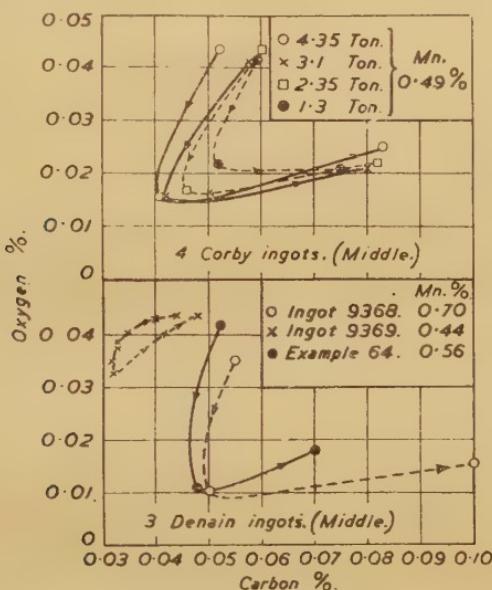


FIG. A.—Carbon-Oxygen Relationships (from Mitchell's papers).

In their introduction they quote the results on Denain ingots and on Corby ingots, but, when reaching their conclusions, they have not considered these figures, which entirely oppose the theory that manganese affects the balanced composition. A few of the results mentioned<sup>1</sup> are plotted in Fig. A, three locations (outside of rim, and rim and core on either side of junction) on the middle sections of the ingots having been selected for simplicity. All the curves, except one, take a wide anti-clockwise sweep and therefore the steels are above the balanced composition, although the carbon contents are low (0.06% or less) and the manganese contents high

<sup>1</sup> J. Mitchell, *Journal of The Iron and Steel Institute*, 1942, No. II., pp. 295 p and 327 p.

(0·49–0·70%). The exception (ingot 9369) is plotted in more detail from the outside of the rim to the inside of the rim/core junction and shows that this steel with 0·044% of carbon and 0·44% of manganese is very near the balanced composition (but still a shade above it). The two low-carbon casts examined by the authors, with about 0·04% of carbon and 0·10% and 0·29% of manganese, are also on or very near the balanced composition.

All the data presented by the authors, with the exception of one individual oxygen figure, are in line with the view that the carbon content of the balanced composition is about 0·04% and that this is not materially altered by the manganese content. The practical import of this conclusion is that all commercial rimming steels not only become partially self-deoxidised in the rim but the core is not enriched in oxygen as a result of the rimming action, being in fact usually also deoxidised to a substantial degree.

Referring to the effect of pressure, in a system under increased pressure a higher product of oxygen and carbon is naturally required to initiate and continue the rimming action. The ratio of oxygen to carbon at the balanced composition would not be altered unless the composition of the reaction products (evolved gas and deposited metal) became altered by the pressure, and there is no proof of this.

If the ferrostatic pressure in the bottom part of an ingot builds up a higher (O)  $\times$  (C) product at the solid/liquid interface, no sign of it remains in the solid ingot, or at least it has not been demonstrated. The (O)  $\times$  (C) product in the core (junction or elsewhere) of a solid ingot decreases from top to bottom. It appears that the effects of segregation more than nullify any effect on the balanced composition that may have been produced during rimming.

The facts outlined in the last half-paragraph of the authors' introduction are explained by the effects of pressure on the vigour of the rimming action and consequently on the composition of the rim, combined with the effects of segregation on the composition of the core.

Dr. D. BINNIE (The Lancashire Steel Corporation, Ltd., Irlam, near Manchester) wrote : The authors have demonstrated that in the writer's paper<sup>1</sup> the pit carbon figure of 0·08% reported was too high and should have been nearer 0·05% of carbon. This pit carbon sample was taken at a time when the writer was unfamiliar with Hultgren and Phragmén's work and no special attention was paid to the procedure now known to be necessary in obtaining a pit carbon value fully representative of the ladle metal. Thus, even if the pit sample were still available the writer would hardly place full reliance on it for the accurate basis of testing a theoretical deduction on the rimming action.

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1942, No. II., p. 283 p.

The writer prefers to catch pit samples for research work in a copper pot and, as in the sampling procedure mentioned in the present paper, containing crumpled aluminium wire.

However, from a position 14 in. from the top of the ingot investigated in his above-mentioned paper, millings,  $\frac{1}{32}$  in. at a time, were cut off, commencing at the outer edge, and analysed for carbon, with the following results :

Cut No.	.	.	1	2	3	4	5	6	7	8
Carbon.	%	:	0.078	0.078	0.070	0.058	0.056	0.056	0.054	0.054

These figures lend support to the view that the pit carbon figure might have been 0.08%, but the writer is aware of the counter-effects of tar on the mould and pick-up which might have rendered this deduction invalid.

The authors have shown that the balanced composition is modified by manganese and pressure, using the much more confirmatory method of oxygen determinations as well as carbon analyses.

I agree with the authors that a single balanced composition does not exist for all parts of the same ingot.

Manganese was selected by the writer in his above-mentioned paper as being the only element present in sufficient quantity to alter appreciably the tilt of the Fe-C-O  $\delta$  liquidus plane, but, of course, in future work on rimming steels it might be better to record the percentage of extraneous metals, such as copper, nickel, &c., which, although perhaps is low in some instances, might yet in others prove of value in future theoretical deductions on the movement of segregation in rimming steel.

Mr. S. W. EVANS (Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd., Cardiff) wrote : This paper forms a further valuable contribution to all the useful work on rimming steel which has been presented during the last few years. In this case it is most satisfying to have such full steelmaking details included.

The sheet trade requires low-carbon rimming steel for deep-drawing purposes, as free as possible from harmful segregation of carbon. This is required so that uniform grain-size results on annealing, following the cold reduction, may be obtained, and that the steel is not stiffened by the metalloids. Given these conditions, very deep pressings can be satisfactorily made. Hence it follows that the difference in carbon content between the rim and core should be as small as possible, without a peak at the junction, which conditions seem to be met with metal on or below the balanced composition. Apart from its theoretical importance, knowledge of the balanced composition is thus of great benefit to the practical steel-maker. The latter then has an upper limit of carbon in the pit sample, above which harmful segregation of carbon is possible. The higher this limit is the better, for time will not then have to be spent in getting down to very low carbon limits. It is therefore

disconcerting to find cast 27/6293, with a pit carbon content of 0·075%, which is in the normal sheet-steel range, to be above the balanced composition, and giving a core carbon figure of 0·11% in the middle of the ingot. According to Table VII., therefore, a maximum pit carbon value of 0·07% should be the aim for deep-drawing steel. This, however, is not in agreement with examination results on other ingots. Several were listed by Binnie,<sup>1</sup> e.g., his own ingot of 0·08% carbon giving 0·045% in the core, ingot No. 61 giving less in the core than the pit sample of 0·08% of carbon, and the ingot of Nead and Washburn with 0·097% in the pit sample and 0·064% of carbon in the core. These three examples fall within the normal sheet limits of 0·30–0·40% of manganese.

Is it not possible that there is another factor concerned in the determination of the balanced composition? Such a factor might possibly be reflected in the rimming action, when it could be evaluated by the steelmaker and so used as a supplementary means of grading ingots prior to rolling into sheet orders. This is prompted by the figures given for the ingot of cast 35/7407. The pit-sample and mid-core carbon figures are the same, but with a manganese content of 0·30% one would expect 0·14% of carbon to be above the balanced composition. There must, however, have been some difference in rimming action between this cast and the other four because of the necessity of adding aluminium. It is presumed that the addition of  $1\frac{1}{2}$  oz. per ton was given for control purposes during teeming, and not, as in the case of cast 31/979, immediately before plating. This is in accordance with the pit-sample carbon-oxygen product, which is in excess of 0·0025, thus putting the steel above the line *YNZO* of Hultgren and Phragmén's diagram.<sup>2</sup> Gas would be evolved in such a case before the rimming action commenced, and the metal would appear to sink, aluminium being given to steady it. In each of the other four cases, the carbon-oxygen product is less than 0·0025, and so some metal would solidify before the mother-liquor became concentrated enough for the product to reach the line *YNZO*. Such differences would surely be apparent in the rimming action during the first few seconds.

With reference to the sulphur print of the slab section from cast 29/9106, the double rim might have been caused in two ways. When the top became completely frozen, the rimming action would slow up as the internal pressure increased. A "break through" of the top crust would release this pressure, when rimming would recommence. It would be very interesting to examine an ingot which in some way had been prevented from freezing over on top for appreciably longer than the normal 20 min. or so. Would the "rim" thickness be appreciably increased? The other possible cause of the formation

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1942, No. II., p. 283 p.

<sup>2</sup> See C. A. Edwards, Ninth Report of the Committee on the Heterogeneity of Steel Ingots, Section II., Fig. 1, *The Iron and Steel Institute*, 1939, Special Report No. 27.

of the double rim might be an aluminium addition. According to Table II., this cannot apply, but if, at some time during the rimming, some aluminium were given, the top might cease boiling for a few seconds, to recommence again. This has been observed when "cooler-plating." It would be interesting to know the precise cause of the double rim, for, according to the sulphur print, it has the effect of decreasing the intense segregation at the junction zone.

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#### AUTHORS' REPLY.

The AUTHORS wrote in reply: We regret that Dr. Dickie's interpretation of the evidence presented in this paper differs from our own, although this was not entirely unexpected. We realise fully that numerous examples from past investigations on rimming steel apparently refute the tentative conclusions reached in the present paper. The exact placing of the Corby ingots and the Denain ingots, and more particularly the ingot examined by Dr. Binnie, has been the subject of considerable study by us. So much depends on accurate sampling and analysis, and, moreover, the balanced composition is so sensitive that slight variations in analysis modify severely the form of the curve. Under these conditions and without casting aspersions on the reported results of other investigators, we felt that we could formulate conclusions only from our own work.

In the paper we have taken as the criterion for the balanced composition the fact that at the balanced composition the steel solidifies without change of composition in the liquid. On this basis, casts 31/979 and 29/9106 are balanced, and we regard the effect of manganese as having been demonstrated in these two samples. That cast 27/6293, with slightly higher carbon but of similar manganese content, should show an "above-balanced" characteristic would suggest either faulty sampling or the effect of other variants.

From a long study of rimming steels it is clear that the "below-balanced" composition rarely occurs in practice and in fact, in this paper, the first two steels cannot be regarded as definitely below-balanced but rather as being just on the balanced composition. By far the larger proportion of commercial steels are of the above-balanced type; consequently, the exact location of the balanced composition is likely to continue to be a debatable point.

In regard to the apparent decrease in the  $(O) \times (C)$  product from top to bottom of an ingot, we consider this effect to be due to ferrostatic pressure. On account of pressure, the lower rim solidifies with more carbon and oxygen than the upper portions, and consequently the lower core contains less oxygen than the upper core. The upper portions will, however, tend to compensate for this by greater loss of carbon monoxide. Finally, superimposed on these

theoretical considerations are the undoubted influence of effects due to turbulence and normal segregation.

We note Dr. Binnie's remarks concerning the pit sample of the ingot discussed in the Appendix, and his further careful carbon determinations at the extreme edge of the ingot slice. These results would appear to offer confirmation of the original pit-sample value. The effect of other elements on rimming phenomena must always be borne in mind.

Mr. Evans' thoughtful contribution gives a useful and practical application to the theory of the balanced composition. We agree that the apparent disparity in the behaviour of the two steels, one with 0·07%, the other with 0·075% of carbon, is due possibly to another factor. Mr. Evans' remarks on the double-rim effect are noted with interest. An excellent example of the production of a double rim resulting from a breakout of the surface was recorded in the discussion of rimming-steel papers at the Autumn Meeting held at Sheffield in 1942.<sup>1</sup> The same effect was observed in certain of the laboratory experiments reported by us in a subsequent paper.<sup>2</sup>

Answering the question put by Mr. Evans, there is ample evidence that if the top of the ingot can be prevented from freezing, the thickness of the rim tends to increase, but there is a limit to which this can be effected in practice.

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1942, No. II., p. 376 p.

<sup>2</sup> *Journal of The Iron and Steel Institute*, 1944, No. I., p. 321 p (this volume).

# A STUDY OF A SHELL-STEEL INGOT.<sup>1</sup>

By D. BINNIE, Ph.D. (THE LANCASHIRE STEEL CORPORATION, LTD., IRLAM, NEAR MANCHESTER).

(Figs. 3 to 63 = Plates XXVII. to XXXII.)

*Paper No. 25/1943 of the Committee on the Heterogeneity of Steel Ingots.*

## SUMMARY.

An ingot of shell steel, teemed uphill and containing 0·47% of carbon and 0·88% of manganese, has been examined in some detail. Information is given on the manufacture of the steel. The sulphur print and analyses at the standard positions of the Committee on the Heterogeneity of Steel Ingots are shown.

Longitudinal sections were cut from the feeder head and from the base of the ingot, and transverse sections from the top, middle and bottom of the ingot proper, all of which were subjected to close examination.

The position of the chill equi-axed crystals, the columnar crystals and the equi-axed crystals behind the columnar crystals are illustrated; these areas have also been photographed after a copper etch, which brings out the dendritic structure.

Among features brought to light is the presence of white spots of precipitated ferrite, seen in all sections of the ingot except the feeder head. The intensity and distribution of these white spots are considered.

The lower half of the ingot had, on sulphur printing, a zoned effect: A light coloured zone at the surface, a dark zone, a light coloured zone and again the normal dark zone of the ingot. This zoning is compared with the acid-etched surface of the metal.

A detailed analysis of the steel throughout the zoning is also given.

At the request of the Committee on the Heterogeneity of Steel Ingots an ingot of shell steel was examined, and information obtained is the subject matter of this paper.

## DETAILS OF THE INGOT.

The ingot (cast 6608) was made by the basic open-hearth process in C furnace in the works of the author's Company. Steelmaking and teeming data are given in Table I.

Particulars of the ingot mould used are given in Fig. 1.

The ingot was selected from the second plate of four ingots; it

<sup>1</sup> Received August 23, 1943. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed are the author's, and are not necessarily endorsed by the Committee as a body.

TABLE I.—*Shell-Steel Ingot. Steelmaking and Teeming Data.**Final Bath Samples.*

Time reported.	C. %.	S. %.	P. %.	Mn. %.	Iron in Slag. %.
2.01 P.M.	0.49	0.034	0.030	0.26	9.5
2.20 P.M.	0.43	0.033	0.026	0.23	...
2.36 P.M.	0.41	0.033	0.025	0.21	10.0

Tapped at 2.45 P.M.

*Tapping Slag.*

SiO <sub>2</sub> . %.	Al <sub>2</sub> O <sub>3</sub> . %.	CaO. %.	MgO. %.	FeO. %.	Fe <sub>2</sub> O <sub>3</sub> . %.	MnO. %.	S. %.	P <sub>2</sub> O <sub>5</sub> . %.	Fe. %.
12.6	1.1	55.9	3.16	6.14	7.15	4.72	0.27	8.48	9.8

*Teeming.*

1½-in. nozzles, twelve 20-in. closed-bottom moulds (3 plates of 4 ingots each). Teemed uphill. Moulds tar-washed.

Anti-piping compound used.

Approximate weight of ingot and head, 3 tons 10 cwt.

*Additions.*

To bath :	Spiegel	2 cwt.
To ladle :	Ferro-silicon	2 cwt. 2 qr.
	Ferro-manganese	8 cwt. 0 qr.
	Aluminium	10 lb.
To moulds :	Aluminium	2 lb. per mould.

*Pit Samples.*

C. %.	Si. %.	S. %.	P. %.	Mn. %.	Ni. %.	Cr. %.	Cu. %.	As. %.
(a) 0.47	0.201	0.033	...	0.87	0.01	0.04	0.09	0.028
(b) 0.47	0.206	0.034	0.035	0.88	...	...	...	...

was cut, planed and polished to expose the section through the vertical axis.

*Polished Surface of the Ingot.*

There was no pipe cavity below the shoulders of the feeder head. The only internal unsoundness was one blow-hole situated on the axis and about one-third up the ingot from the bottom. Subcutaneous blow-holes were present along the very bottom of the ingot, but apart from these the ingot, including the surface, was free from unsoundness.

*Sulphur Print of the Ingot.*

The sulphur print of the ingot is reproduced in Fig. 3. It reveals the following features :

V-segregates were pronounced and extended two-thirds down the axis of the ingot. Λ-segregates were also present over this region.

The surface portions of this uphill-teemed ingot extending to about half-way up the ingot and gradually running out showed a zoned effect : A light zone on the sulphur print, ½ in. wide at the bottom of the ingot; then a dark zone of a tint similar to that of the main print, about the same width with a white central streak

dividing the zone into two; then another white zone about  $\frac{1}{4}$  in. wide, behind which the sulphur print was normal in tint.

In the lower portion of the sulphur print dendrites could be seen passing unrestrictedly through these zones.

The runner-feed for the ingot showed up as a clear-cut area, an area which was accentuated by the light and dark zones of the ingot surface in this region.

Dendrites were developed throughout the ingot and some well-defined examples were seen at the *F* and *G* standard ingot positions as well as close to the surface. The feeder-head portion was highly dendritic.

### *Analysis of the Ingots.*

The ingot was drilled at standard positions, as shown in Fig. 2.<sup>1</sup> The results are collected in Table II.

### *The Ingot Sections Examined.*

From the portion of the ingot that was not used for sulphur-printing sections were cut, as follows, for detailed examination:

*Ingot Section No. 1.*—Vertical section of the feeder-head portion. The surface examined would be about  $\frac{1}{2}$  in. from the axis of the ingot.

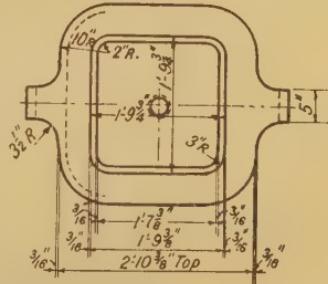
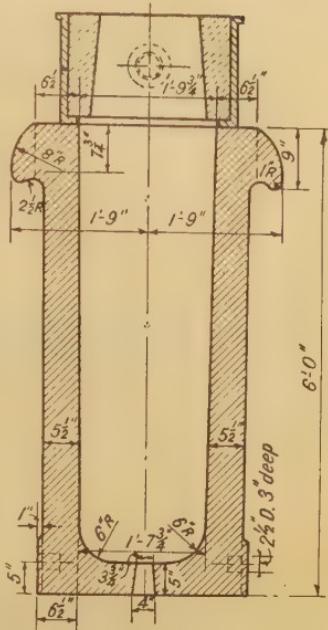


FIG. 1.—Dimensions of the Ingot Mould Used.

TABLE II.—*Shell-Steel Ingot. Analyses at the Standard Positions (Fig. 2).*

Position.	C. %.	Sl. %.	S. %.	P. %.	Mn. %.
A . . .	0·470	0·206	0·032	0·035	0·89
B . . .	0·430	0·201	0·030	0·0315	0·88
C . . .	0·435	0·196	0·034	0·035	0·90
D . . .	0·490	0·192	0·033	0·0345	0·90
E . . .	0·700	0·182	0·065	0·065	0·91
F . . .	0·477	0·204	0·035	0·035	0·89
G . . .	0·460	0·204	0·033	0·0345	0·91
H . . .	0·590	0·194	0·042	0·0435	0·88

<sup>1</sup> Fourth Report on the Heterogeneity of Steel Ingots, *The Iron and Steel Institute*, 1932, Special Report No. 2, p. 8.

*Ingot Section No. 2.*—Transverse section at the junction of the feeder head.

*Ingot Section No. 3.*—Transverse section at the middle height of the ingot.

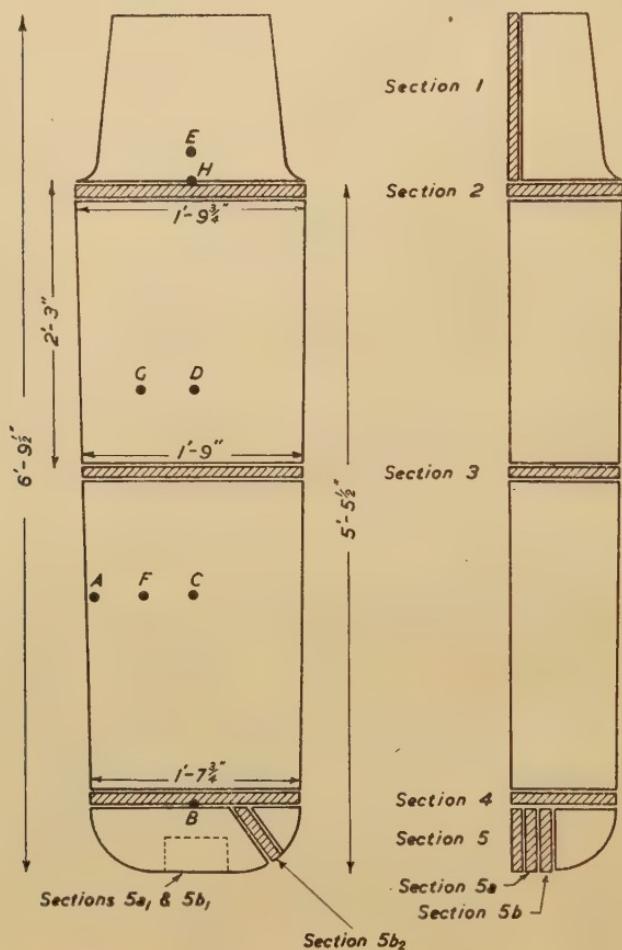


FIG. 2.—Standard Positions for Analysis and Location of Sections Examined.

*Ingot Section No. 4.*—Transverse section from the bottom of the straight portion of the ingot, just where the rounding off at the base begins.

*Ingot Section No. 5.*—Vertical section through the rounded portion of the bottom of the ingot, close to the axis.

All the above sections were sulphur-printed and etched, and

micrographs were taken to show the structure at the outer zones and also, except in the feeder-head slice, at the portion nearest to the centre of the ingot.

The positions of the sections relative to the ingot are shown in Fig. 2.

#### INGOT SECTION No. 1.—VERTICAL SECTION THROUGH THE FEEDER HEAD.

##### *Macro-examination.*

The sulphur print is shown in Fig. 4 and the same surface etched with a macro-etching reagent in Fig. 5. The sulphur print brings out the dendritic structure of this steel and shows the path followed by the sulphide-rich streaks which correspond to the  $\Lambda$ -segregates in the main ingot. Referring to Fig. 5, the  $\Lambda$ -segregate is seen to be a junction line between families of dendrites, as if freezing occurred locally, the  $\Lambda$ -segregate line being the junction between two zones freezing separately.

##### *Micrographs of the Ingot Structure.*

Specimens were cut from 2 in. from the top right-hand corner of the feeder head (Fig. 5). The acid etch, Fig. 6, shows the structure from the mould side of the feeder head; Fig. 7 is a copper etch of the same area, made with a view to bringing out a background of grain.

Fig. 8, an acid etch, depicts the structure at the same position but from the inside of the feeder head towards the mould. Fig. 9, a copper etch, is of the same area as Fig. 8, again showing up a background of steel grain.

The full length of the specimen cut was 2 in., of which 0·8 in. is shown in Fig. 6 and also in Fig. 8. There was no special feature in the intermediate area not photographed, the smaller grain of Fig. 6 passing gradually to the larger grain of Fig. 8.

The micrographs show some decarburisation at the surface (Fig. 8). There is a complete absence of columnar crystals.

The copper etch shows that dendrites persist right to the surface, rather masked by the carburised area, but nevertheless still present.

#### INGOT SECTION No. 2.—TRANSVERSE SECTION AT THE JUNCTION OF THE FEEDER HEAD.

##### *Macro-examination.*

The sulphur print, Fig. 10, shows sulphur spottiness in the area corresponding to the central portion of the ingot, also some blotched areas nearer to but still well away from the surface. Some well-defined dendrites are present, all pointing towards the centre of the ingot.

The macro-etch, Fig. 11, gives a more detailed view of the

dendrites and shows them to be in a more scattered distribution. The dendrites are present throughout the section, but are more marked in an area midway between the surface and the centre of the ingot.

#### *Micrographs of the Ingot Structure.*

Specimens were cut from a portion corresponding to the top left-hand corner of Fig. 11, and thus represent a position midway between the ingot corners.

Fig. 12, acid etch, and Fig. 13, copper etch, on the same surface correspond, on the left-hand side, to the outside skin of the ingot. Some decarburisation and equi-axed crystals are seen at the skin, but the structure quickly passes to columnar crystals and then quite suddenly into equi-axed crystals, 0·45 in. from the surface. The whole surface is peppered with white spots of ferrite, which seem in this instance to be perhaps a little more prevalent in the columnar-crystal zone.

Fig. 14, acid etch, is a continuation of Fig. 12; the right-hand side of this micrograph is 1·75 in. inwards from the skin of the ingot. The grains are much larger, the white spots of ferrite much fewer, but on passing into the steel (the right-hand side of the micrograph) the grains become larger and the white spots tend to disappear.

The intermediate area between Fig. 12 and Fig. 14 did not show any particular feature. The smaller grain size of the right-hand side of Fig. 12 developed gradually into the larger grain size on the left of Fig. 14.

The copper etch of this surface, Fig. 15, shows a slightly larger configuration of the dendrites, where the grains are larger than in Fig. 13.

Figs. 16 and 17 are an acid etch and a copper etch, respectively, on a specimen cut from the centre of the ingot. Segregation of carbon has occurred at this position. The copper etch shows more clearly than the other copper etches from this ingot slice a darker pathway running along the middle of the white areas. Possibly these dark pathways are concentration zones within the cored zone and correspond to ferritic boundaries.

The crack at the bottom of Fig. 17 was caused by mechanical rupture when the ingot was split open.

#### INGOT SECTION NO. 3.—TRANSVERSE SECTION AT THE MIDDLE OF THE INGOT.

#### *Micro-examination.*

Fig. 18 is the sulphur print of this section and Fig. 19 the macro-etch of the same section. A few spots are seen in the inner zones of the sulphur print; the macro-etch shows the steel to be very solid, and the dendrites are not so large as in Figs. 5 and 11.

Figs. 20 and 21 are enlargements of a portion of the sulphur print and of the macro-etch, and show more clearly the change in crystal structure on passing from the surface inwards. The right-hand side of Fig. 20 is the bottom of the middle portion of Fig. 18, and that of Fig. 21 is the top portion midway between the ingot surface and the centre of Fig. 19.

#### *Micrographs of the Ingot Structure.*

Specimens were cut from the top left-hand corner of the transverse slice shown in Fig. 19.

The acid etch, Fig. 22, shows that at the skin there is a thin layer of chill crystals but no decarburisation; the structure quickly passes into columnar crystals, which persist throughout the range of Fig. 22. Fig. 24 is a continuation of Fig. 22; the distance between the two photographs is 0.36 in.

The white spots of ferrite abound in Fig. 22 and persist in Fig. 24, except over the last row of columnar crystals, in which they are few in number; this occurs at an ingot depth of 1.38 in. The white spots increase again in the equi-axed zone. Figs. 23 and 25, the copper etches of the surface in Figs. 22 and 24, show a more directional distribution of the dendrites (Fig. 25). Within a range of 0.125 in. the structure shown on the right of Fig. 24 passes into the equi-axed structure in Fig. 26, the centre of the ingot.

Figs. 26 and 27 are from the centre of the ingot as before.

#### INGOT SECTION NO. 4.—TRANSVERSE SECTION AT THE BOTTOM OF THE INGOT.

##### *Macro-examination.*

The sulphur print is shown in Fig. 28. The zoning at the surface of the steel—a white zone, a dark zone with a white streak running through it, a white zone, and then the main mass of steel—is clearly seen. Dendrites pass through these zones unrestrictedly. Subcutaneous blow-holes are visible on this section and are confined to the outer light zone.

The macro-etch, Fig. 29, gives only a suggestion of zoning. Massive dendrites are not so conspicuous as in similar sections from positions further up the ingot. These dendrites are confined to an area nearer to the surface of the steel, although some of them find their way to the surface.

##### *Micrographs of the Ingot Structure.*

Specimens were cut from the top right-hand corner of Fig. 29, macro-etch, see Figs. 30 and 32. The equi-axed chill crystals extend more deeply, 0.33 in., into the steel than in the section higher up the ingot; the columnar crystals persist into the steel to a depth of 1.8 in. A very few white spots are present throughout the equi-axed chill crystals; they are absent in the first part of the

columnar crystals. A narrow belt of white spots parallel to the ingot skin is readily seen running down roughly through the transition zone between the equi-axed and columnar crystals. The spots are again sensibly absent from the columnar zone for a further distance of 0·2 in., then they abound, gradually thinning out deeper into the steel, as can be seen in Fig. 32, which is a continuation of Fig. 30 with only the thickness of a hand hack-saw cut between them. The right side of Fig. 32 is 1·75 in. deep into the steel.

Figs. 31 and 33 are copper etches made on the same surfaces as the acid etches shown in Figs. 30 and 32, the etching being carried out to reveal the background of crystal contours.

An acid etch and a copper etch of a section cut from within  $\frac{1}{2}$  in. of the centre of the ingot at this transverse slice, *i.e.*, from the protuberance left by the parting tool when the ingot was cut (Fig. 29), are shown in Figs. 34 and 35. The acid etch shows normal equi-axed grains, the copper etch non-directional dendrites. The white areas on the copper etch (Fig. 35) again show a central pathway, probably caused by a concentration gradient and outlining the ferritic boundary.

#### INGOT SECTION No. 5.—VERTICAL SECTION AT THE BOTTOM OF THE INGOT.

##### *Macro-examination.*

This section was a vertical slice cut close to the axis of the ingot and included the very bottom of the ingot, rising to a height corresponding to the horizontal cut No. 4.

The sulphur print is shown in Fig. 36. The remarks on the zoning, described in reference to Fig. 28, apply equally here. The zoning runs regularly right along the bottom of the ingot. The subcutaneous blow-holes are confined to the outer zone, and the acid etch, Fig. 37, reveals otherwise very solid metal.

A portion from the right-hand side of the acid etch has been macro-etched and is shown in Fig. 38. This copper etch reveals that the heavier dendrites are confined to an area nearer to the surface than they are further up the ingot, also that in certain instances they pass right up to the surface of the ingot. There is a suggestion that the zoning, so clearly shown in the sulphur print, is present in the copper etch, but careful measurement shows that there is no actual correlation. Lines concentric with the surface curvature sweep round this copper-etched surface; also, at the very bottom of the ingot a multiplicity of another set of lines parallel to the surface and to a depth of about  $\frac{1}{4}$  in. into the ingot can be detected.

An enlargement of a portion of the top left-hand corner of the sulphur print in Fig. 36 is shown in Fig. 41, and confirms that the dendrites pass in and out of the zones unrestrictedly. The boundary between the first and outer light and dark zones is clearly defined.

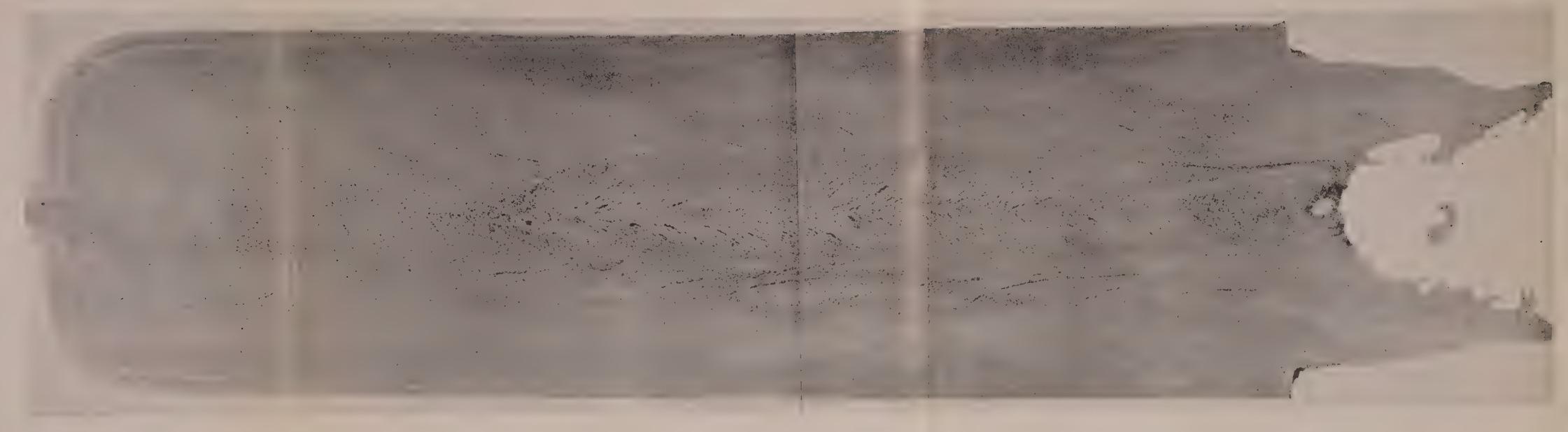


FIG. 3.—Sulphur Print of the Ingots.

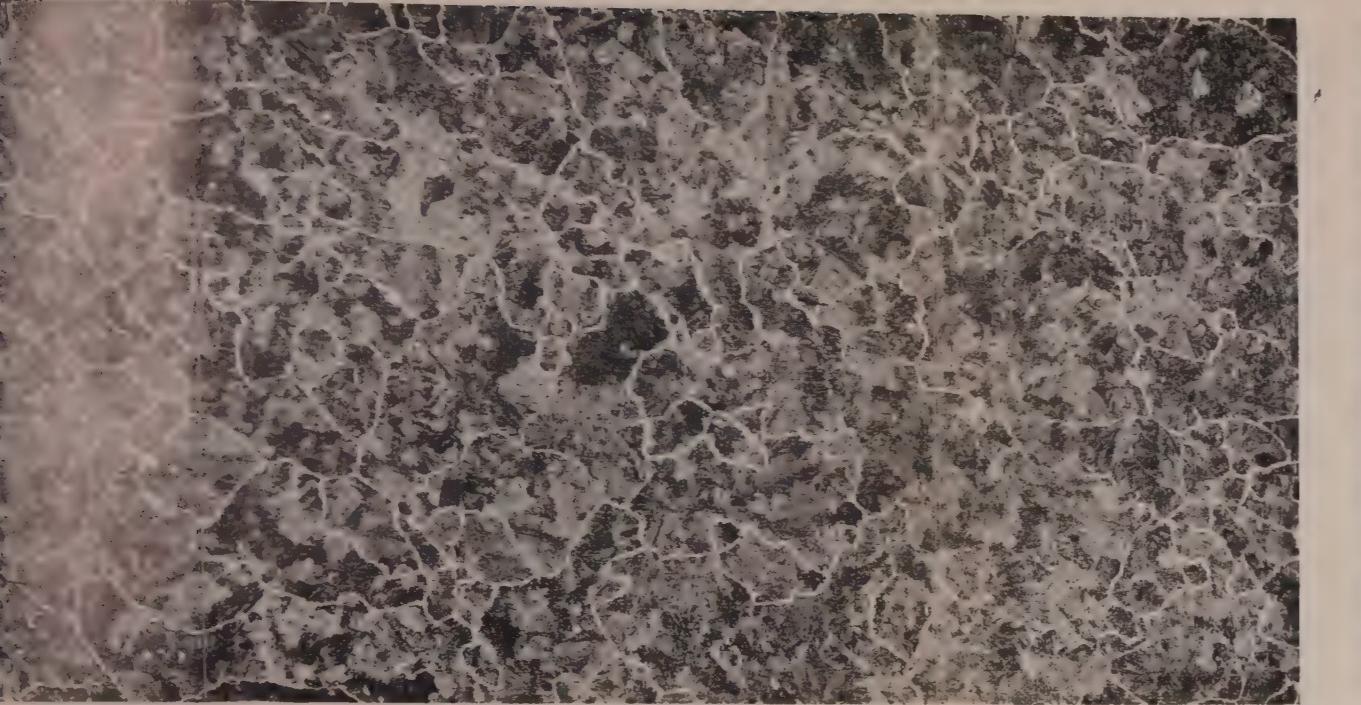


FIG. 4.—Sulphur Print of Feeder Head.  $\times \frac{1}{2}$  approx.



FIG. 5.—Macro-etch of Feeder Head.  $\times \frac{1}{2}$  approx.





-Acid Etch of Feeder Head. Mould side on left.  $\times 15$ .

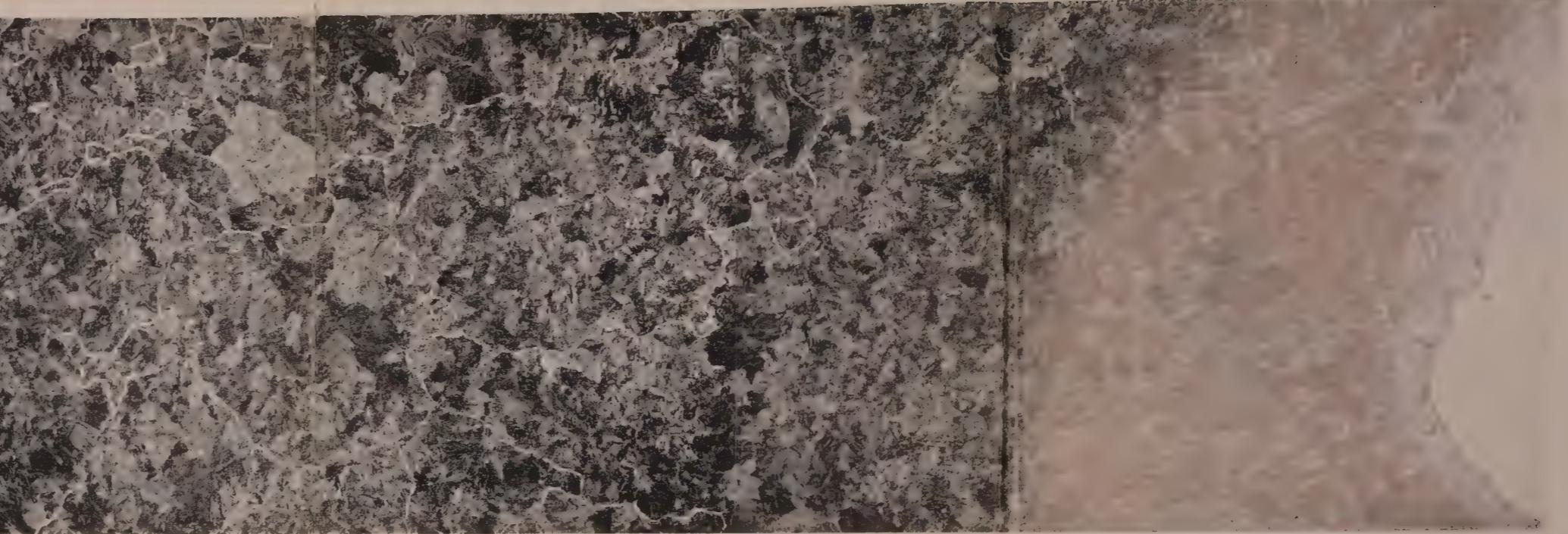


FIG. 8.—Acid Etch of Feeder Head. Cavity side on right.  $\times 15$ .



FIG. 7.—Copper Etch of Surface in Fig. 6.  $\times 15$ .

(Proportions reduced to four-fifths linear in reproduction.)



FIG. 9.—Copper Etch of Surface in Fig. 8.  $\times 15$ .



FIG. 10.—Sulphur Print of Transverse Section of Top of Ingot.  $\times \frac{1}{2}$  approx.



FIG. 11.—Macro-etch of Surface in Fig. 10.  $\times \frac{1}{2}$  approx.

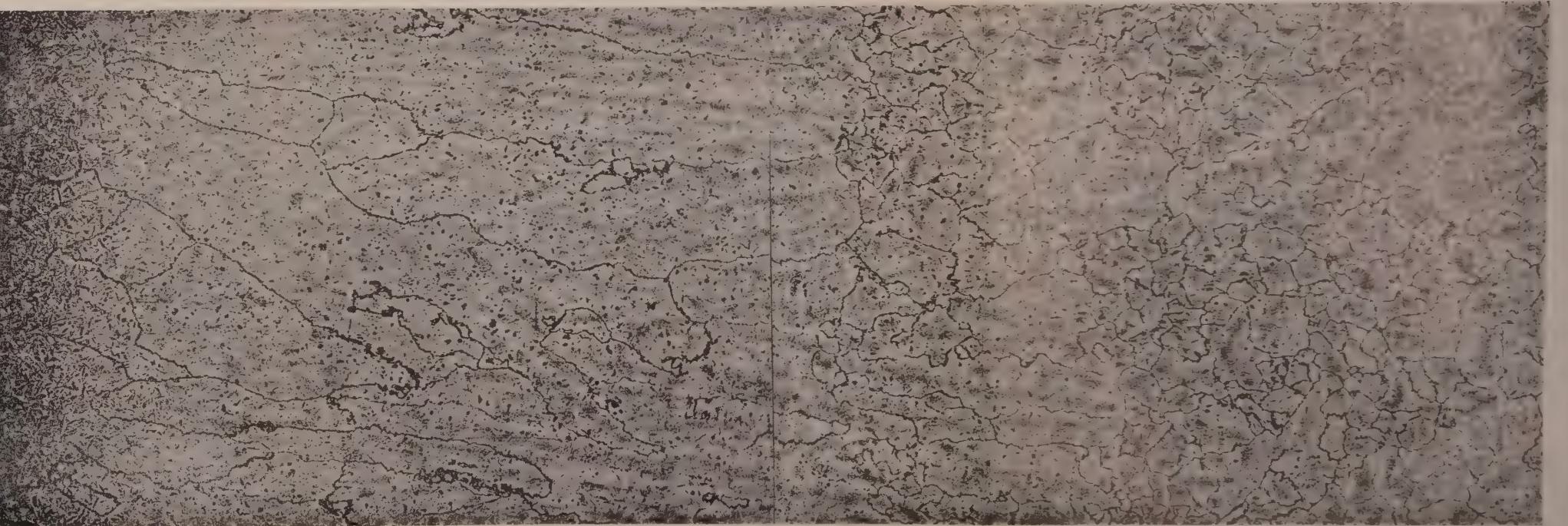


FIG. 13.—Copper Etch of Surface in Fig. 12.  $\times 15$ .

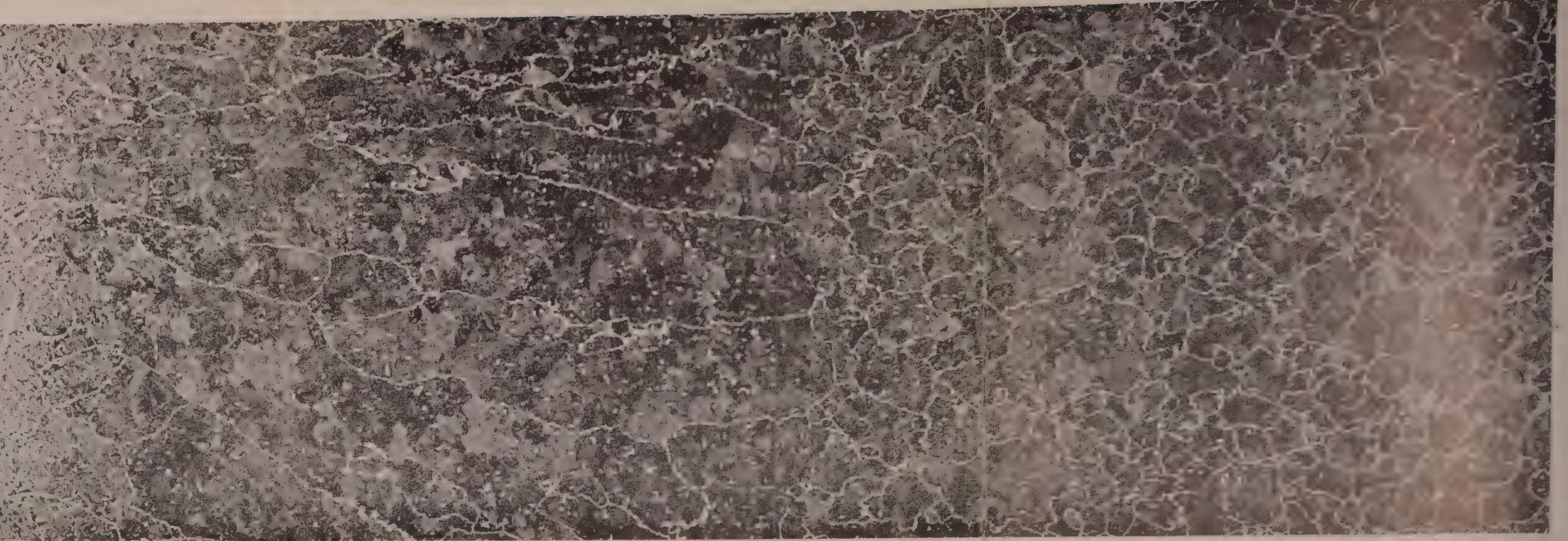


FIG. 12.—Acid Etch of Transverse Section of Top of Ingot. Ingot skin on left.  $\times 15$ .

(Illustrations reduced to four-fifths linear in reproduction)

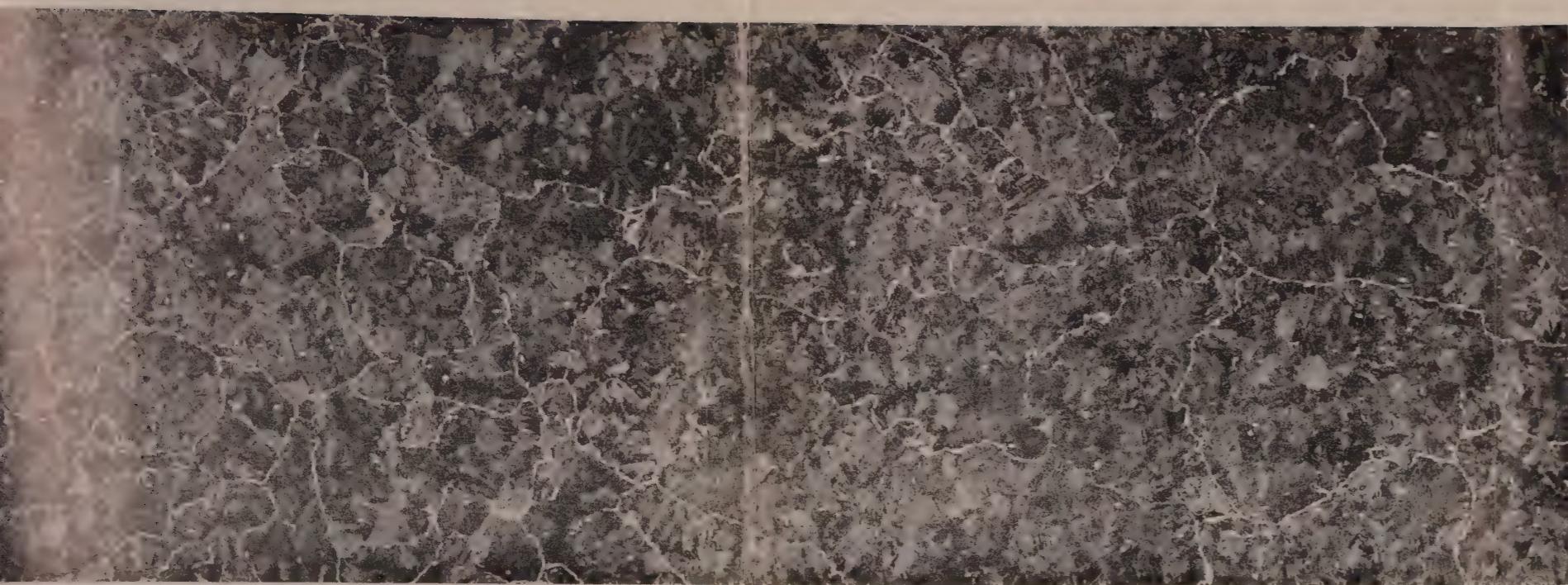


FIG. 14.—Acid Etch of Surface. Continuation of Fig. 12.  $\times 15$ .

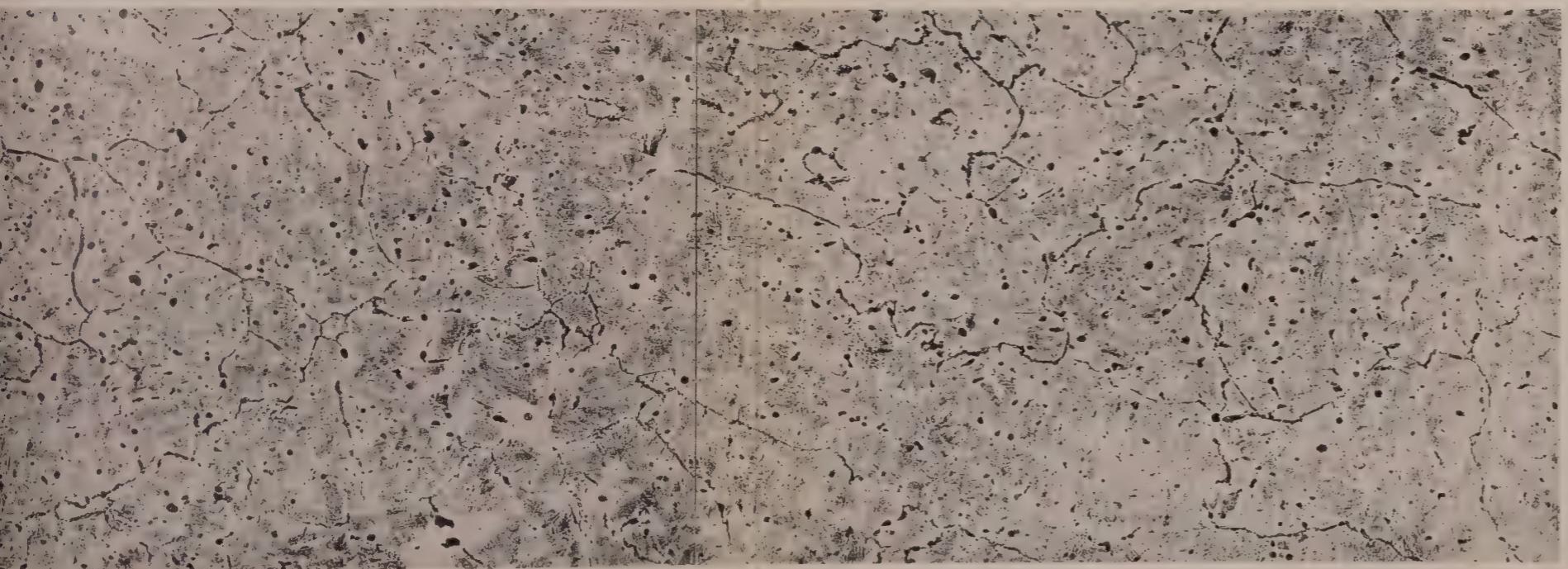


FIG. 15.—Copper Etch of Surface in Fig. 14.  $\times 15$ .



FIG. 16.—Acid Etch of Centre of Ingot, trans. 1 in. of ingot.  $\times 15$ .

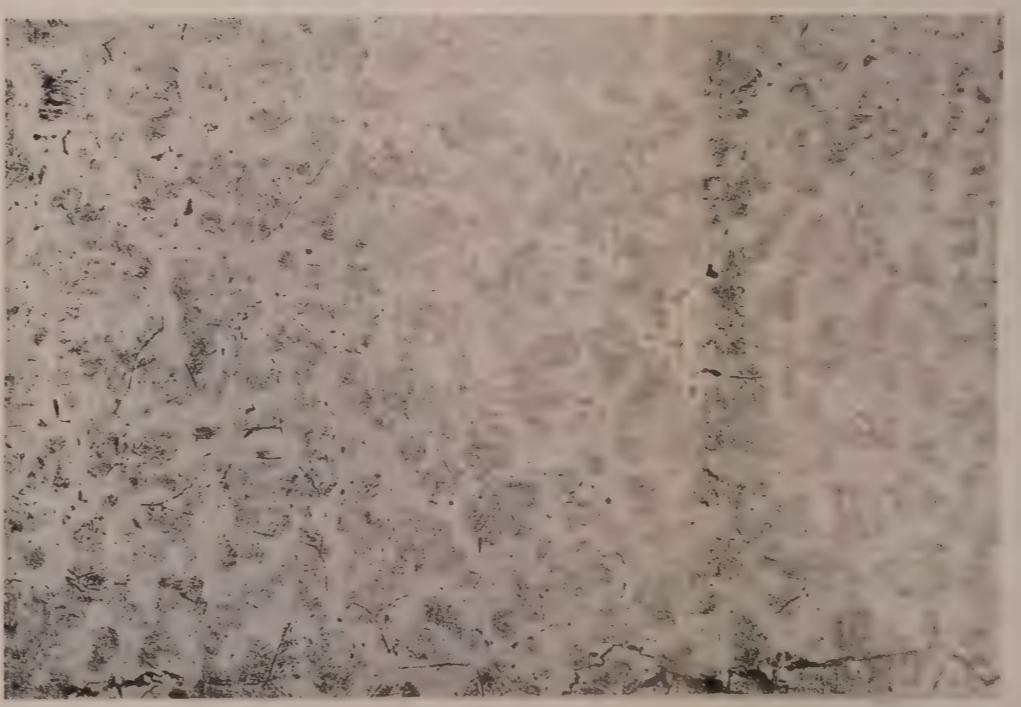


FIG. 17.—Copper Etch of Centre of Ingot in Fig. 16.  $\times 15$ .

[Binnie.



FIG. 19.—Macro-etch of Surface in Fig. 18.  $\times \frac{1}{2}$  approx.



FIG. 18.—Sulphur Print of Transverse Section at Middle of Ingot.  $\times \frac{1}{2}$  approx.



FIG. 20.—Enlargement of Portion of Sulphur Print in Fig. 18.  $\times 3\frac{1}{2}$  approx.



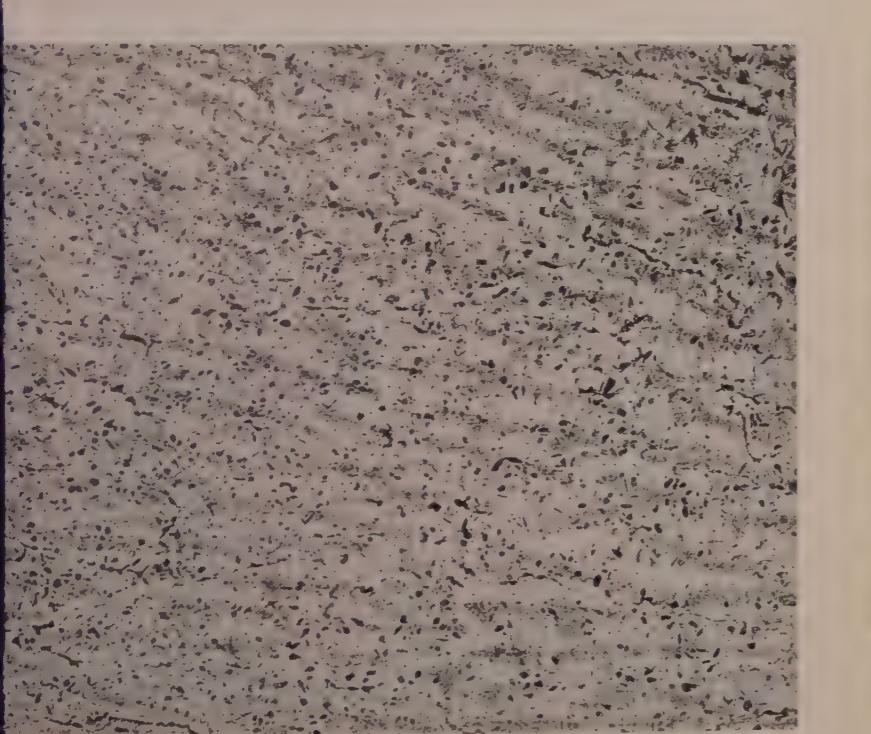
FIG. 21.—Enlargement of Portion of Macro-etch in Fig. 19.  $\times 3\frac{1}{2}$ .



FIG. 23.—Copper Etch of Surface in Fig. 22.  $\times 15$ .



FIG. 22.—Acid Etch of Transverse Section at Middle of Ingot. Ingot



in on left.  $\times 15$ .

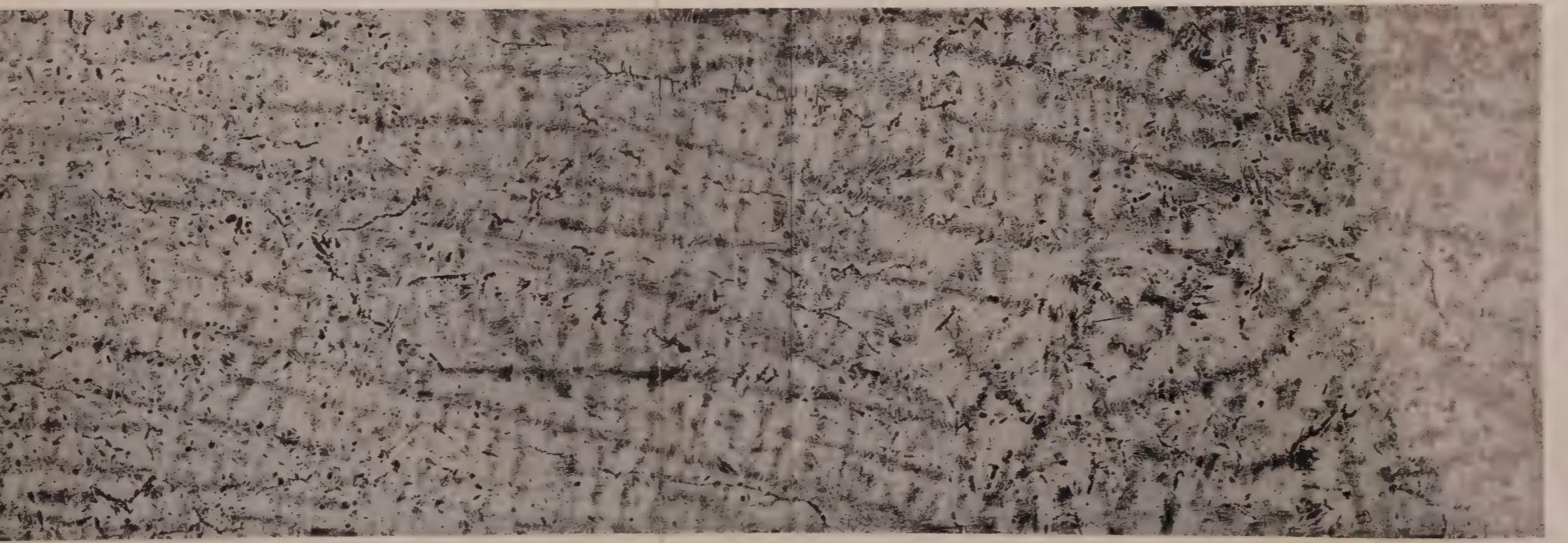


FIG. 24.—Acid Etch of Surface. Continuation of Fig. 22.  $\times 15$ .

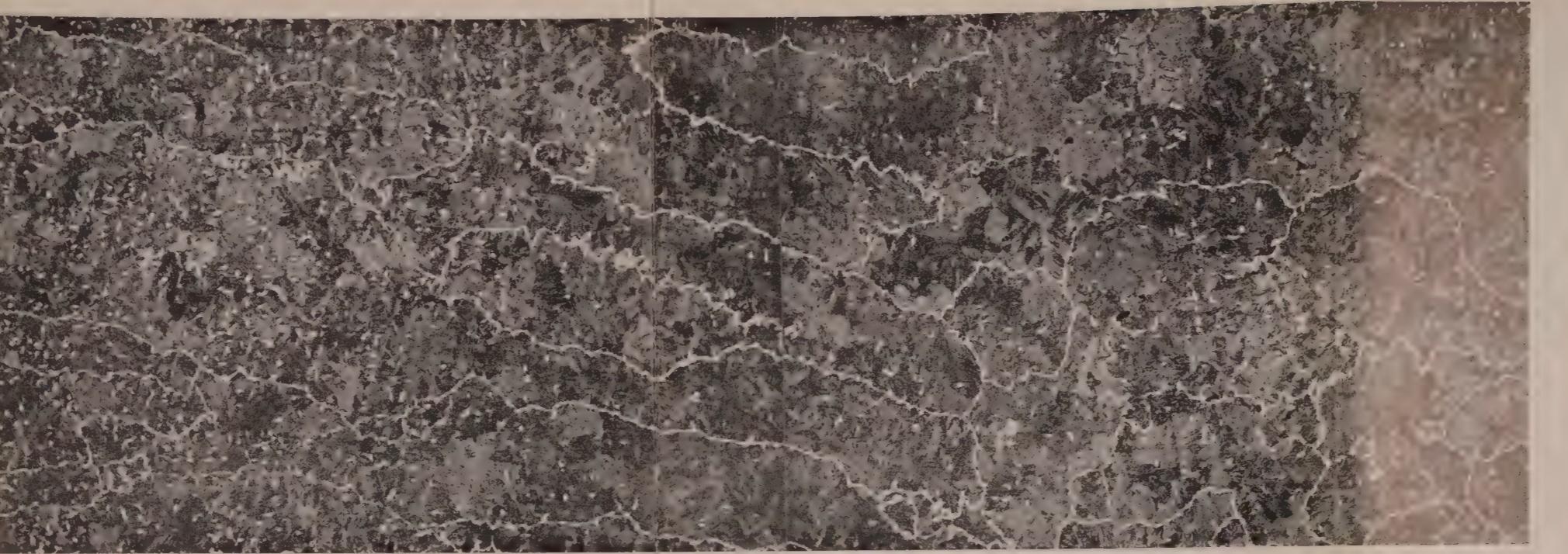


FIG. 24.—Acid Etch of Surface. Continuation of Fig. 22.  $\times 15$ .

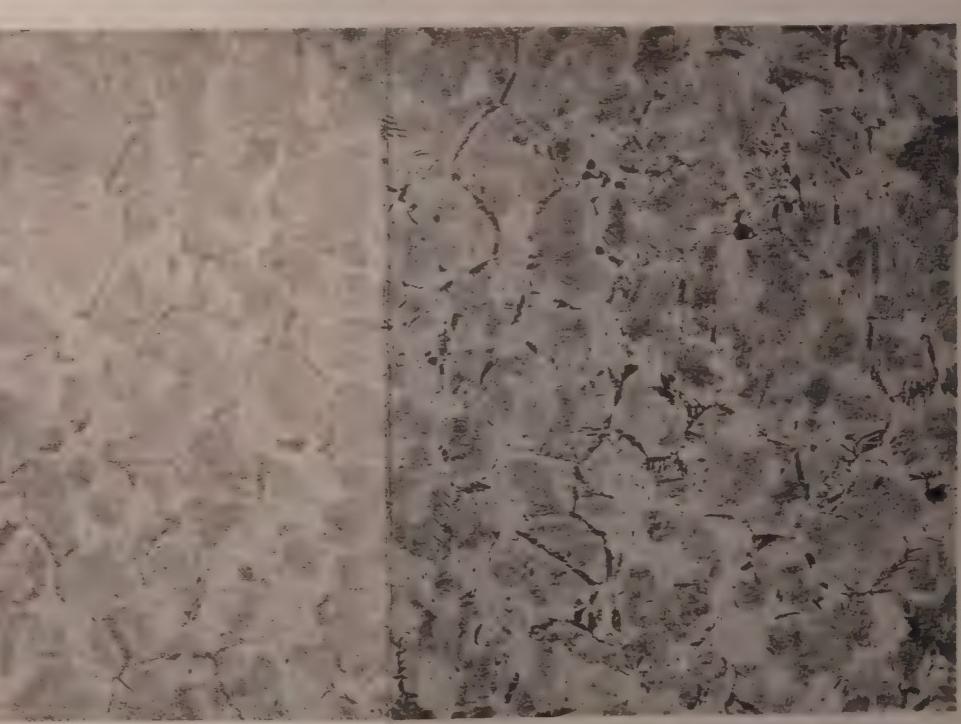


FIG. 25.—Copper Etch of Surface in Fig. 24.  $\times 15$ .



FIG. 26.—Acid Etch of Centre of Ingot; transverse section, middle of ingot.  $\times 15$ .

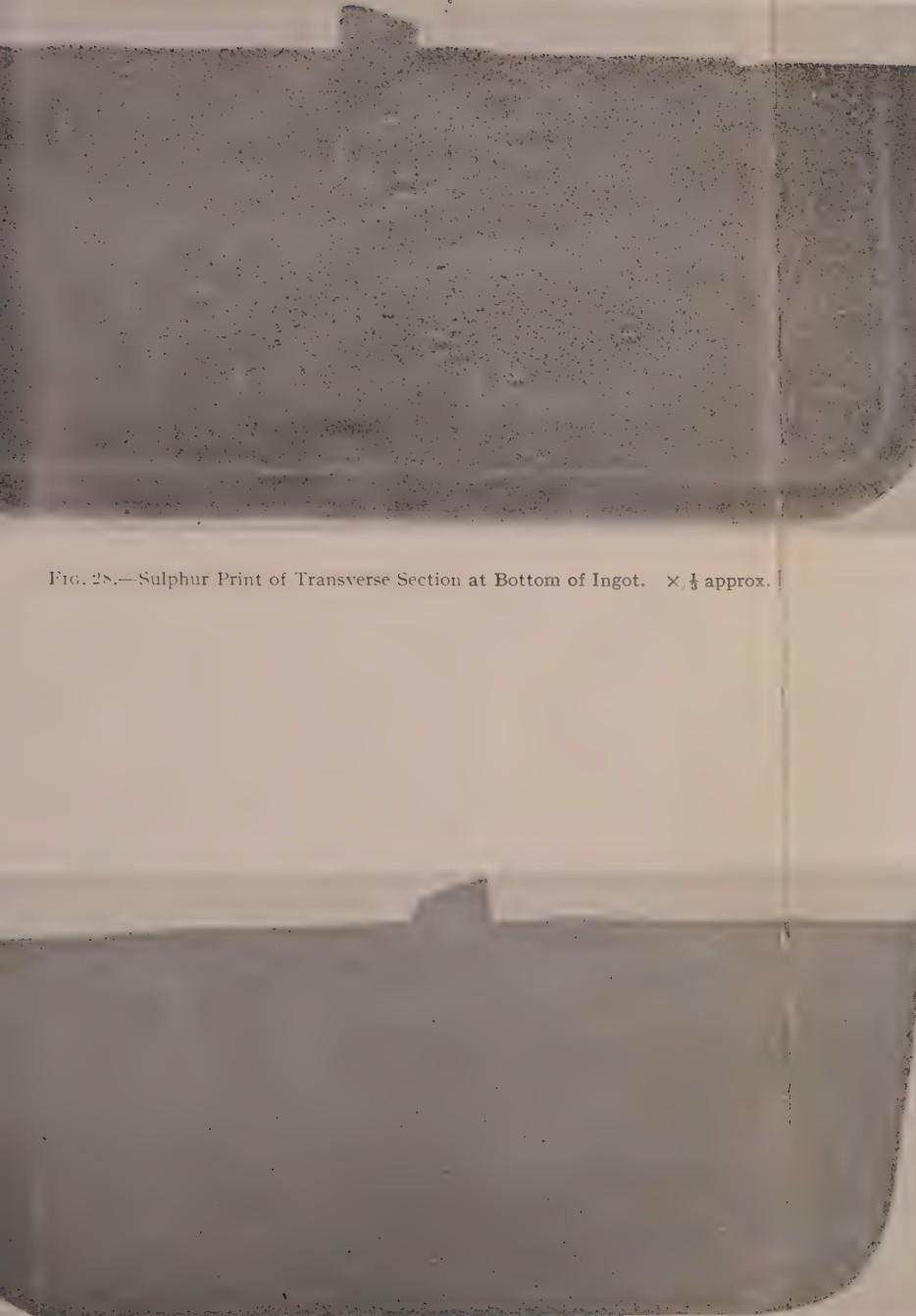


FIG. 28.—Sulphur Print of Transverse Section at Bottom of Ingot.  $\times \frac{1}{2}$  approx.

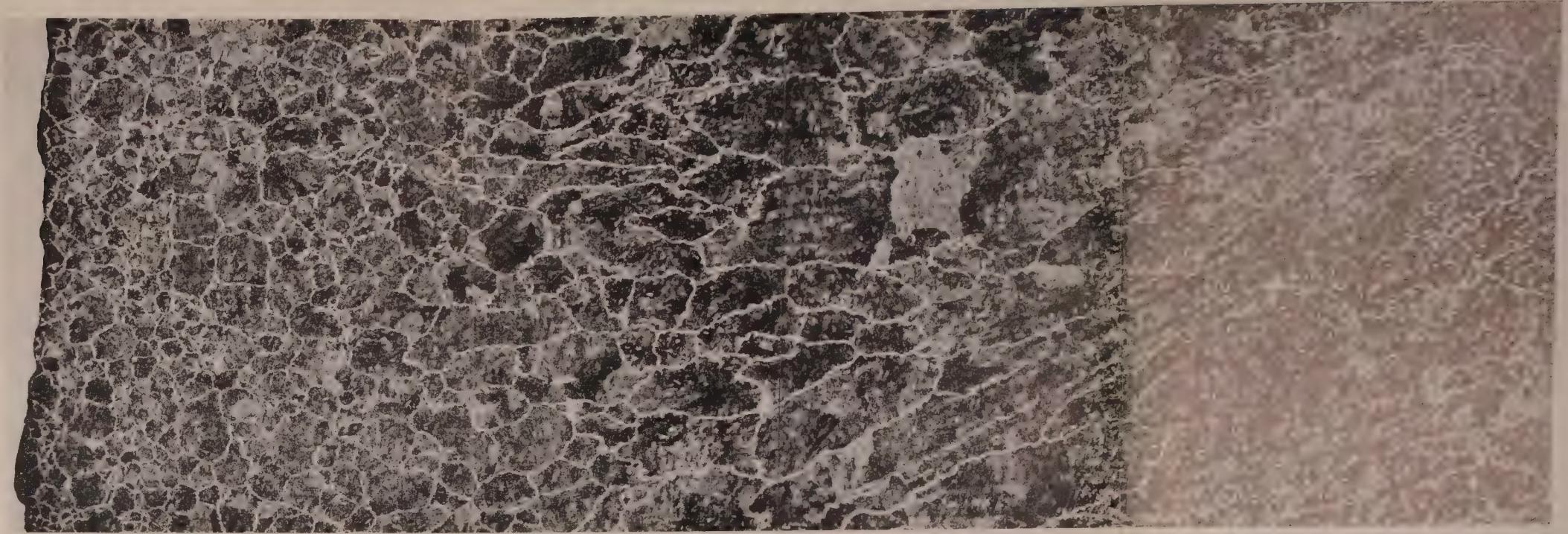


FIG. 30.—Acid Etch of Transverse Section at Bottom of Ingot. Ingot skin on left.  $\times 15$ .

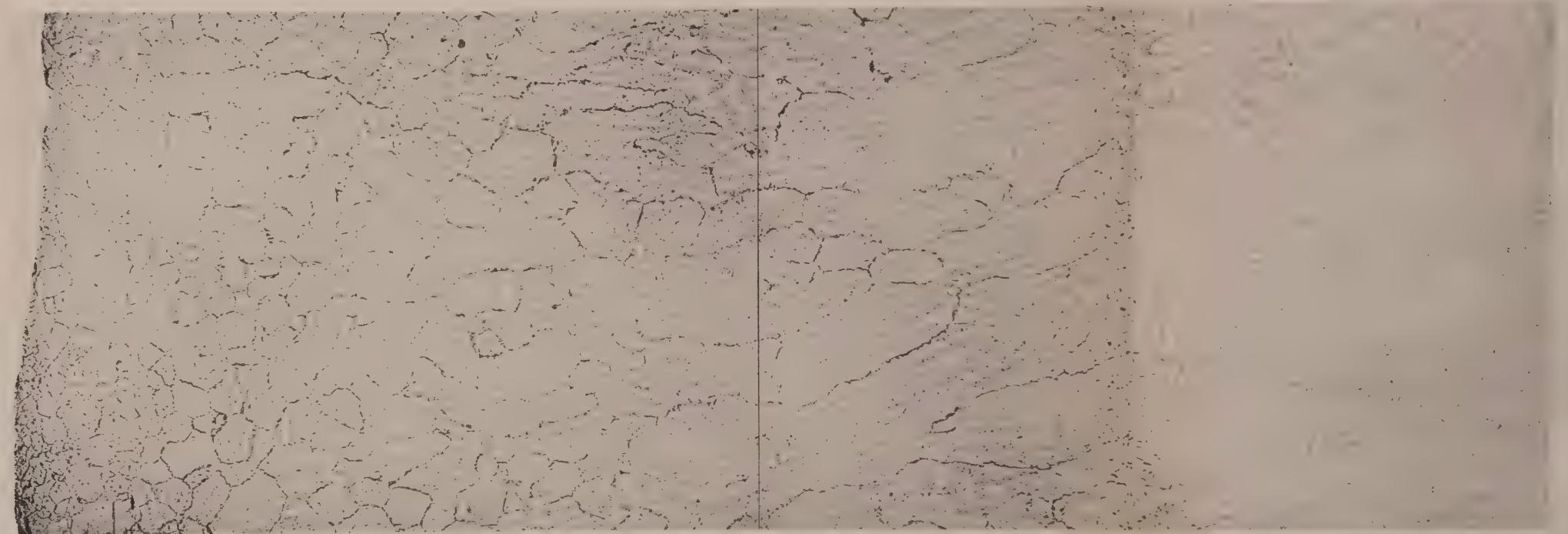


FIG. 31.—Copper Etch of Surface in Fig. 30.  $\times 15$ .

(Illustrations reduced to four-fifths linear in reproduction.)

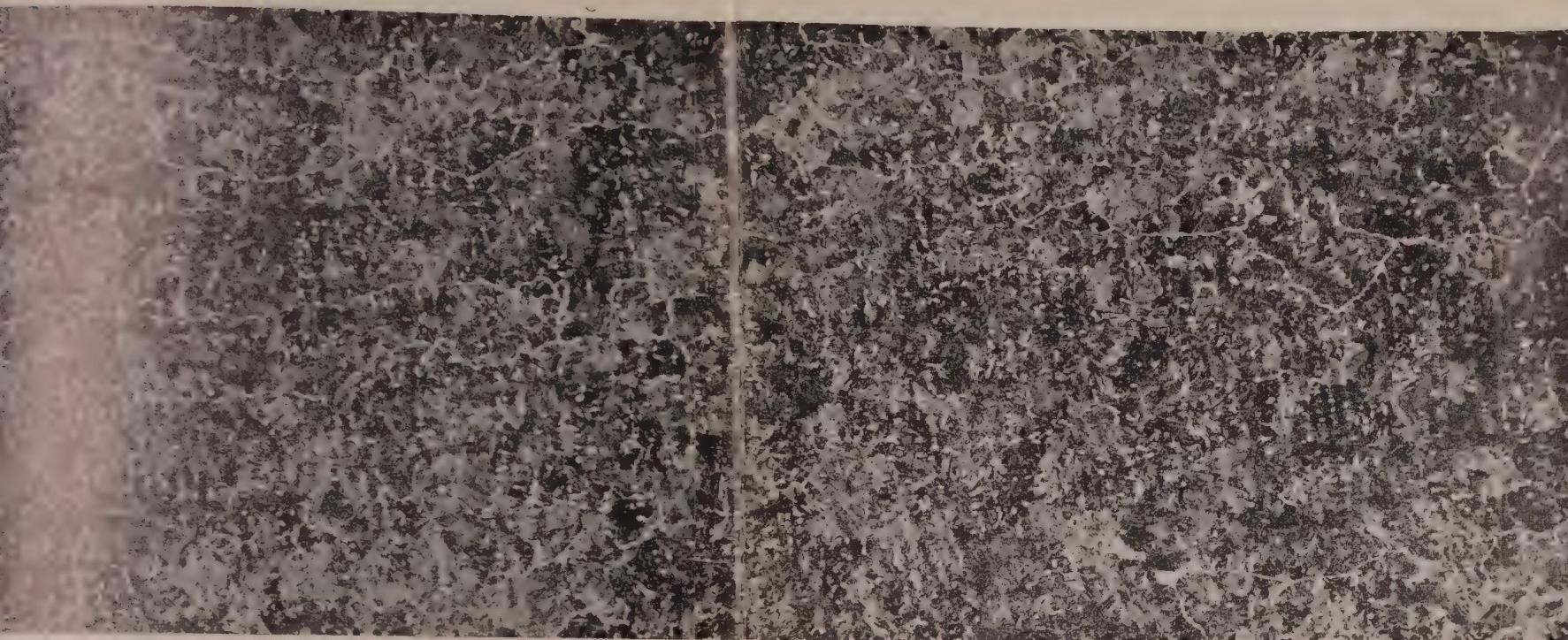


FIG. 32.—Acid Etch of Surface. Continuation of Fig. 30.  $\times 15$ .

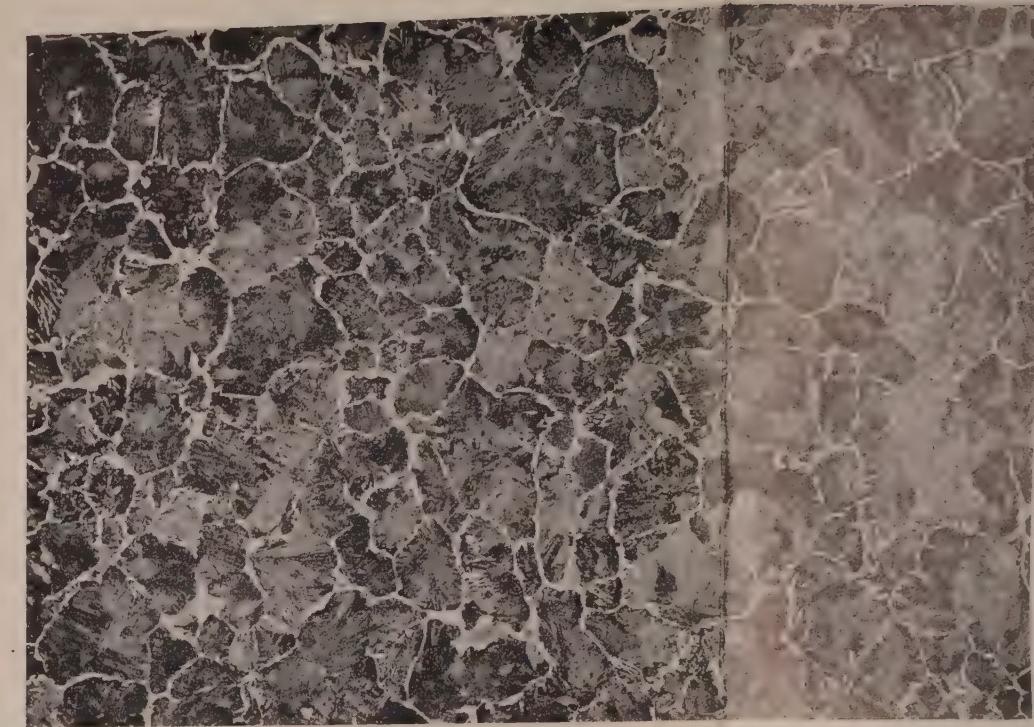


FIG. 34.—Acid Etch of Centre of Ingot; transverse section, bottom half.  $\times 15$ .

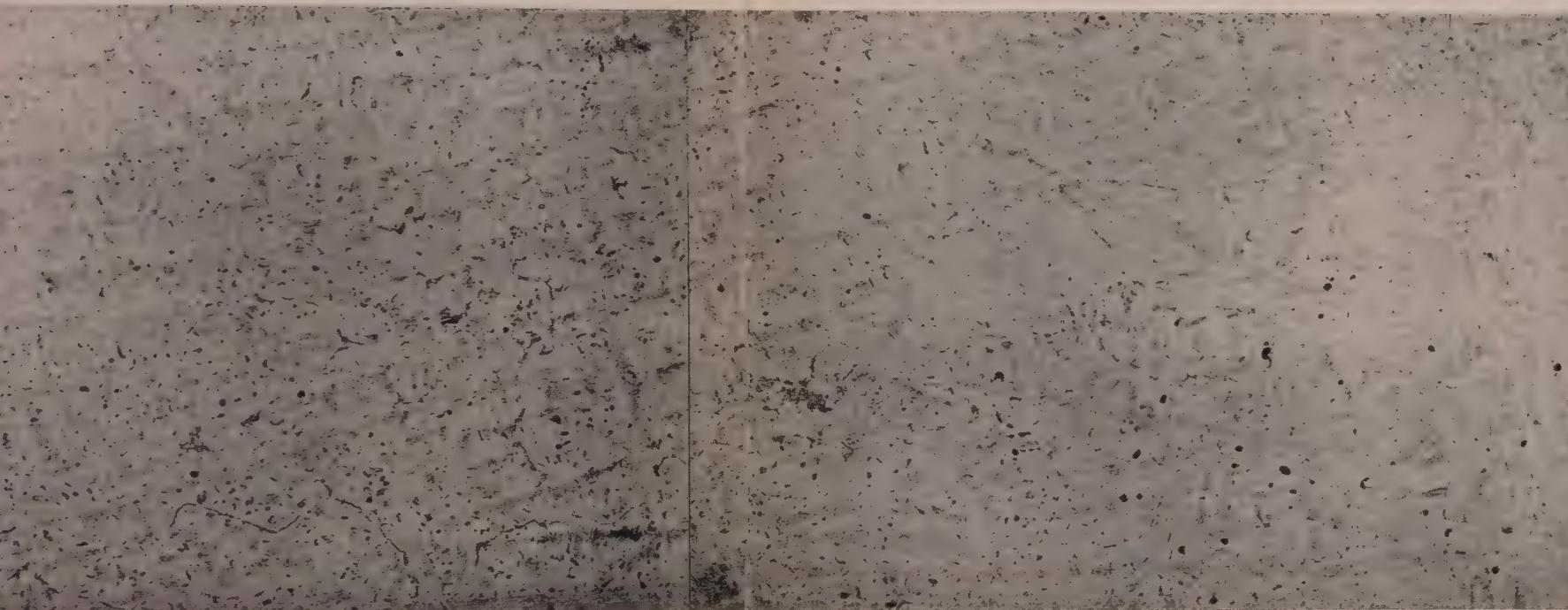


FIG. 33.—Copper Etch of Surface in Fig. 32.  $\times 15$ .

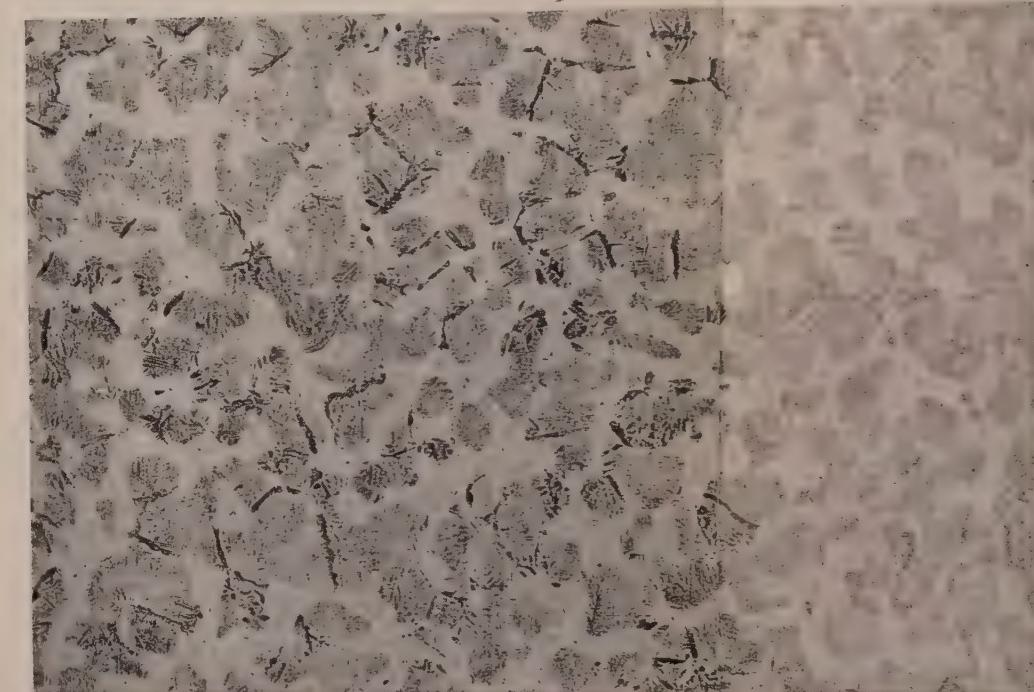


FIG. 35.—Copper Etch of Centre of Ingot in Fig. 34.  $\times 15$ .

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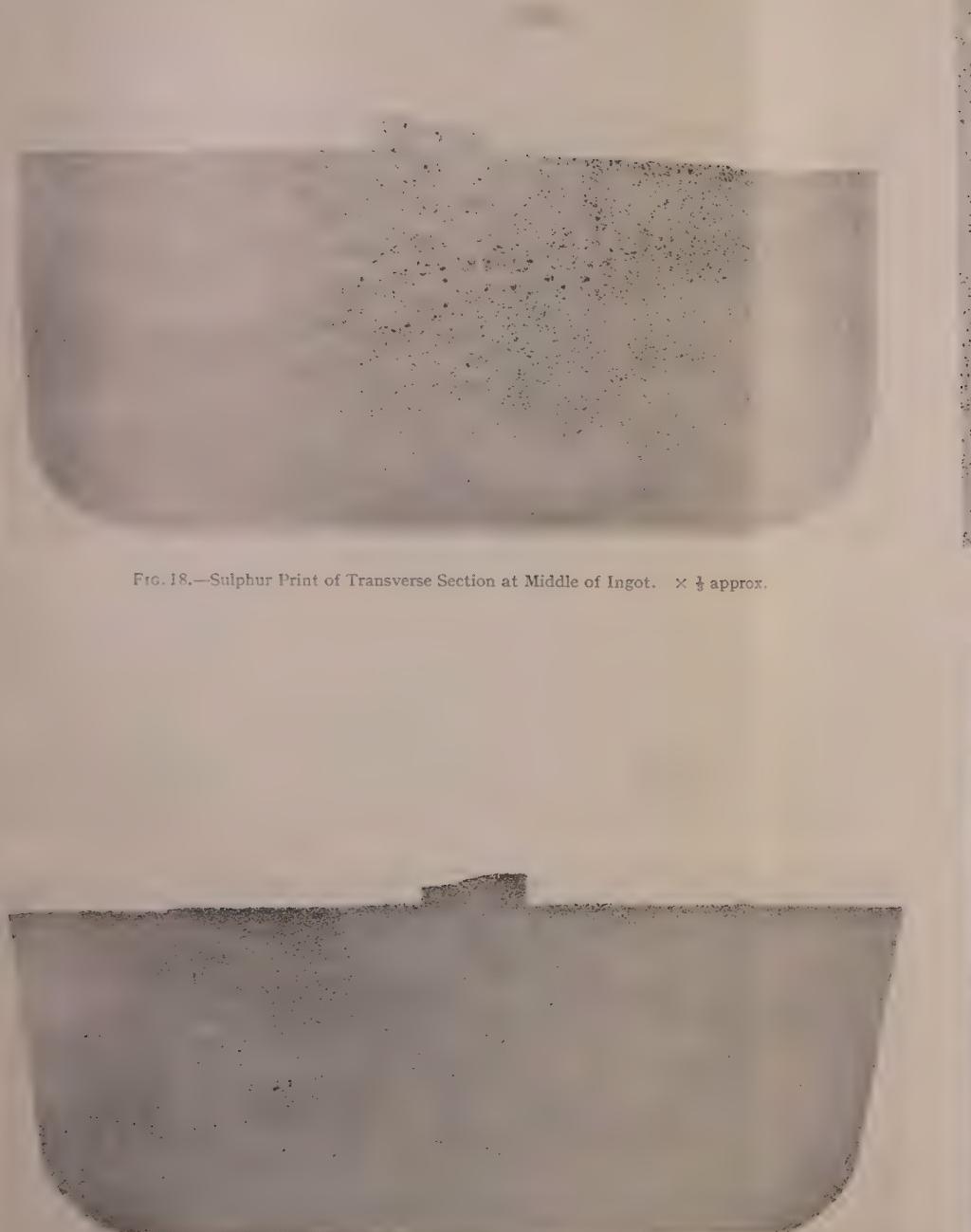


FIG. 18.—Sulphur Print of Transverse Section at Middle of Ingot.  $\times \frac{1}{2}$  approx.



FIG. 20.—Enlargement of Portion of Sulphur Print in Fig. 18.  $\times 3\frac{1}{2}$  approx.



FIG. 22.—Acid Etch of Transverse Section at Mid

ingot skin on left.

$\times 15$ .



FIG. 19—Macro-etch of Surface in Fig. 18.  $\times \frac{1}{2}$  approx.

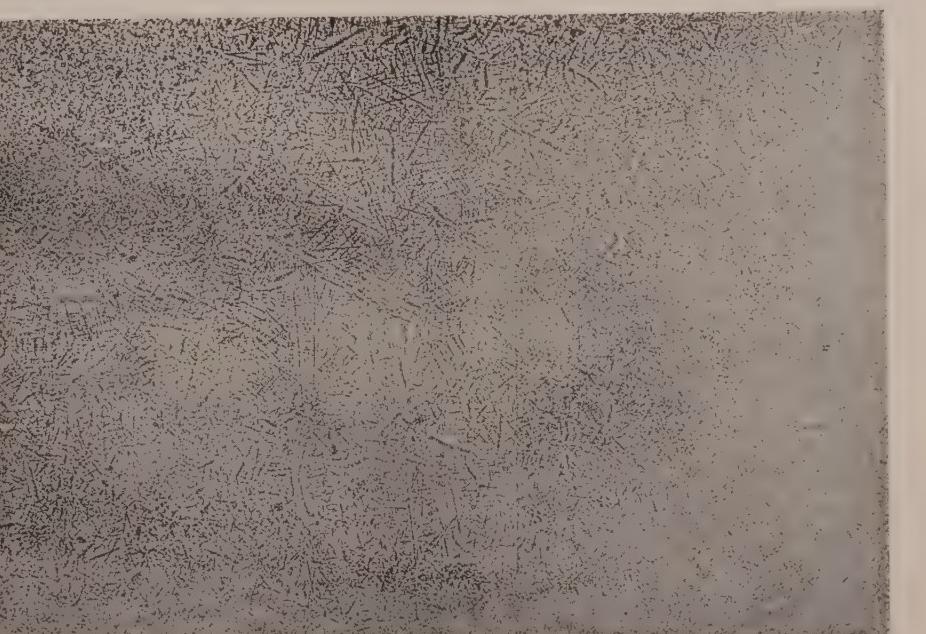


FIG. 21.—Enlargement of Portion of Macro-etch in Fig. 19.  $\times 3\frac{1}{2}$ .

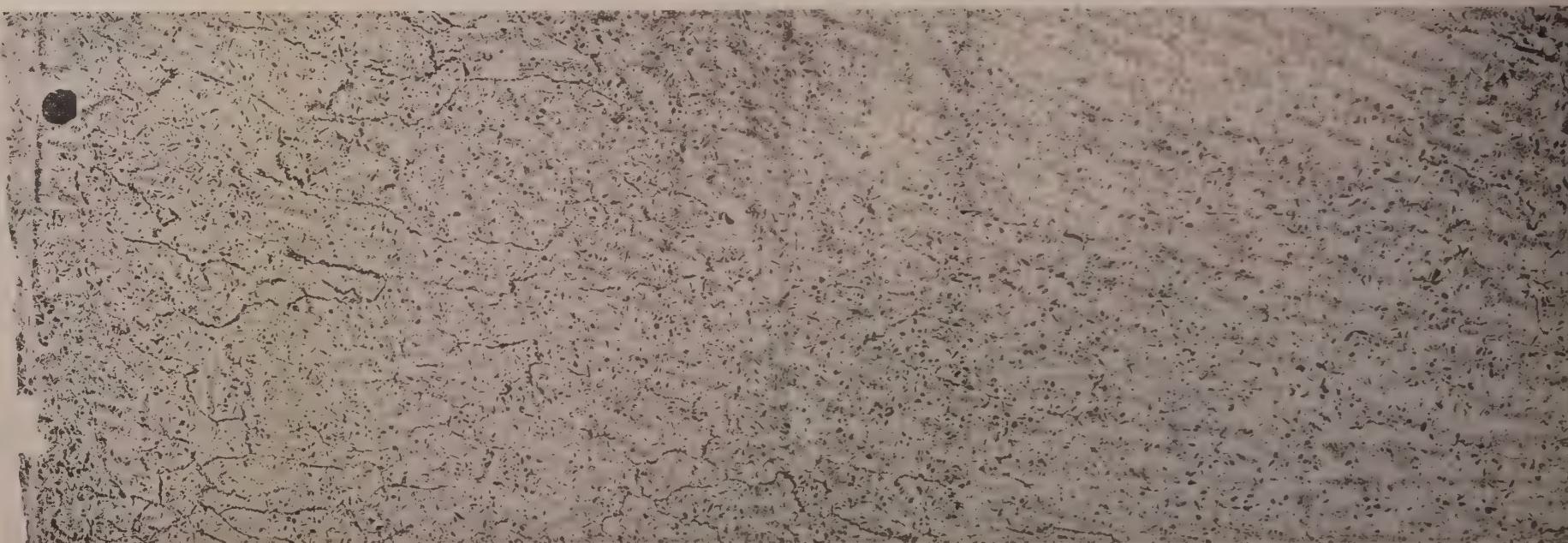


FIG. 23.—Copper Etch of Surface in Fig. 22.  $\times 15$ .

(Illustrations reduced to four-fifths linear in reproduction.)

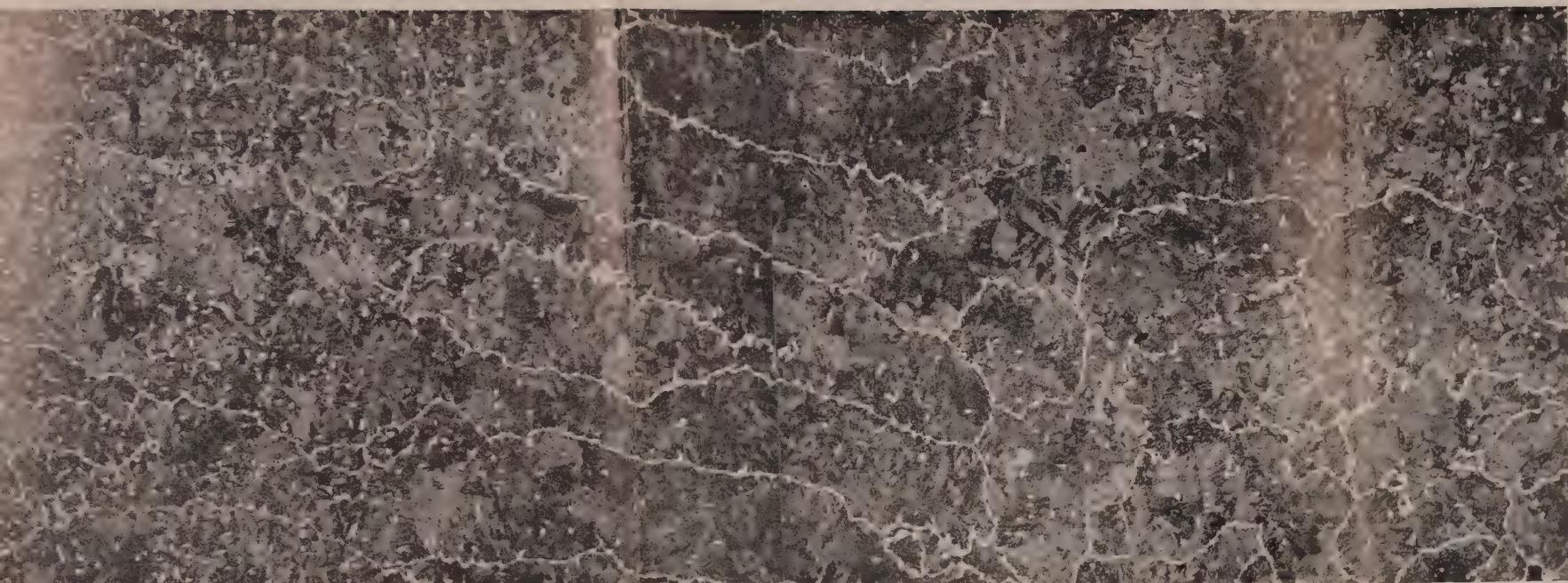


FIG. 24.—Acid Etch of Surface. Continuation of Fig. 22.  $\times 15$ .



FIG. 26.—Acid Etch of Centre of Ingot; transverse section, middle of ingot.  $\times 15$ .

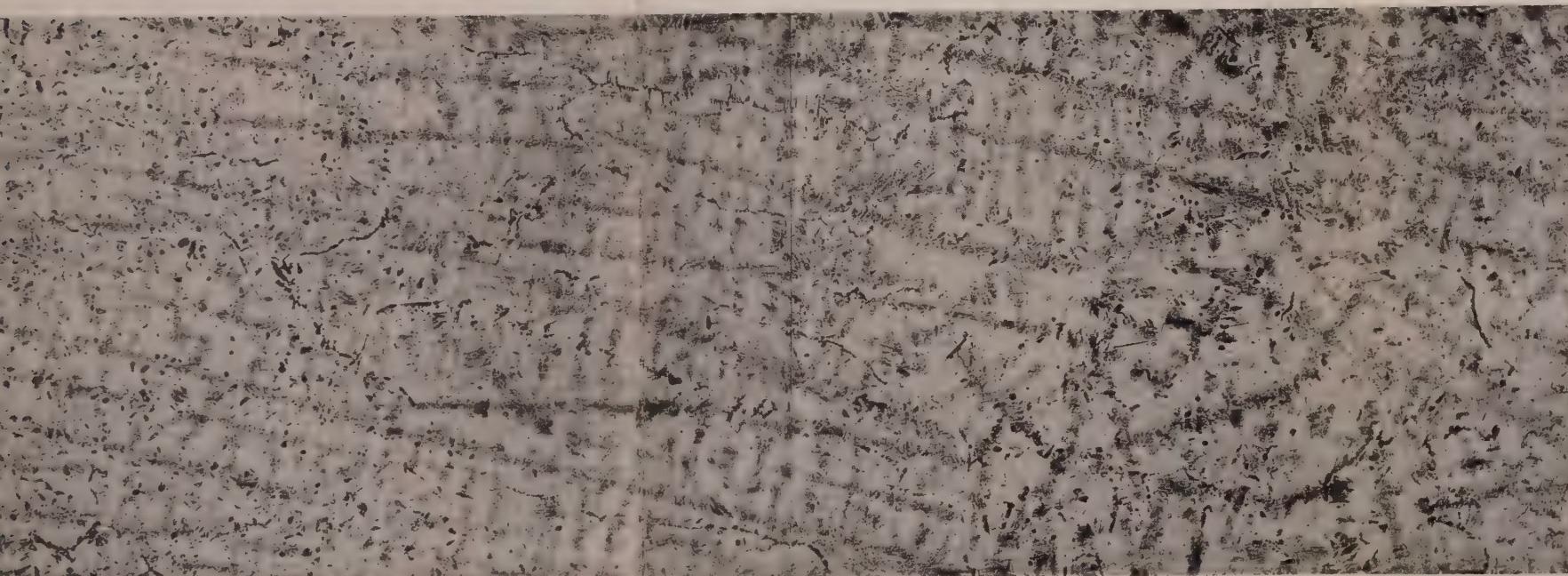


FIG. 25.—Copper Etch of Surface in Fig. 24.  $\times 15$ .

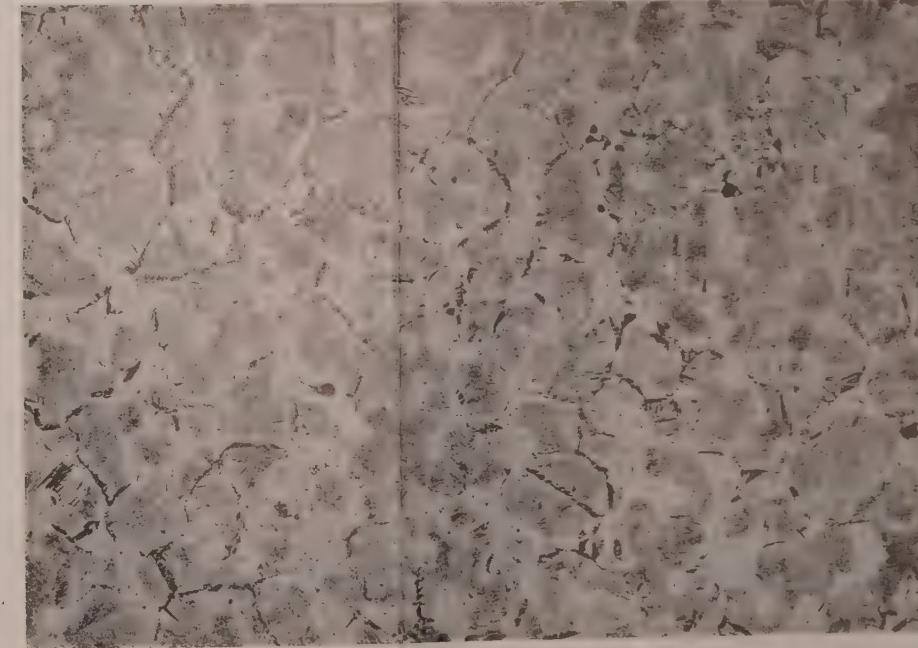


FIG. 27.—Copper Etch of Centre of Ingot in Fig. 26.  $\times 15$ .



FIG. 28.—Sulphur Print of Transverse Section at Bottom of Ingot.  $\times \frac{1}{2}$  approx.

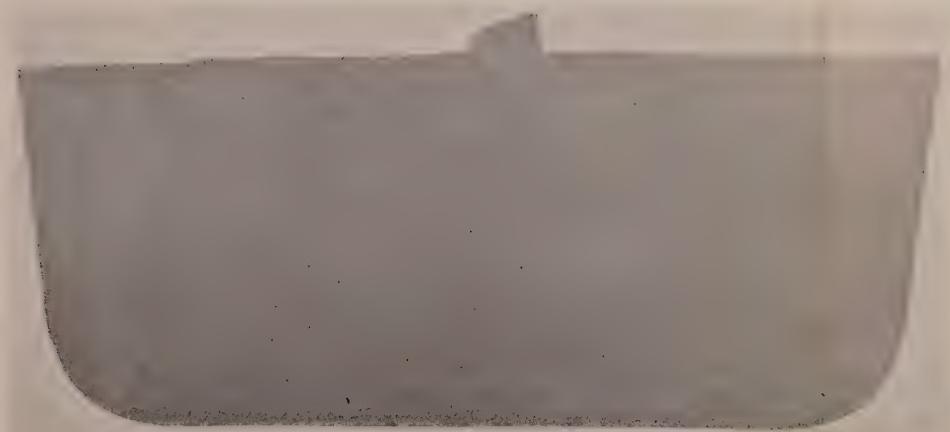


FIG. 29.—Macro-etch of Surface in Fig. 28.  $\times \frac{1}{2}$  approx.



FIG. 30.—Acid Etch of Transverse Section at Bottom of Ingot. Ingot skin on left.  $\times 15$ .

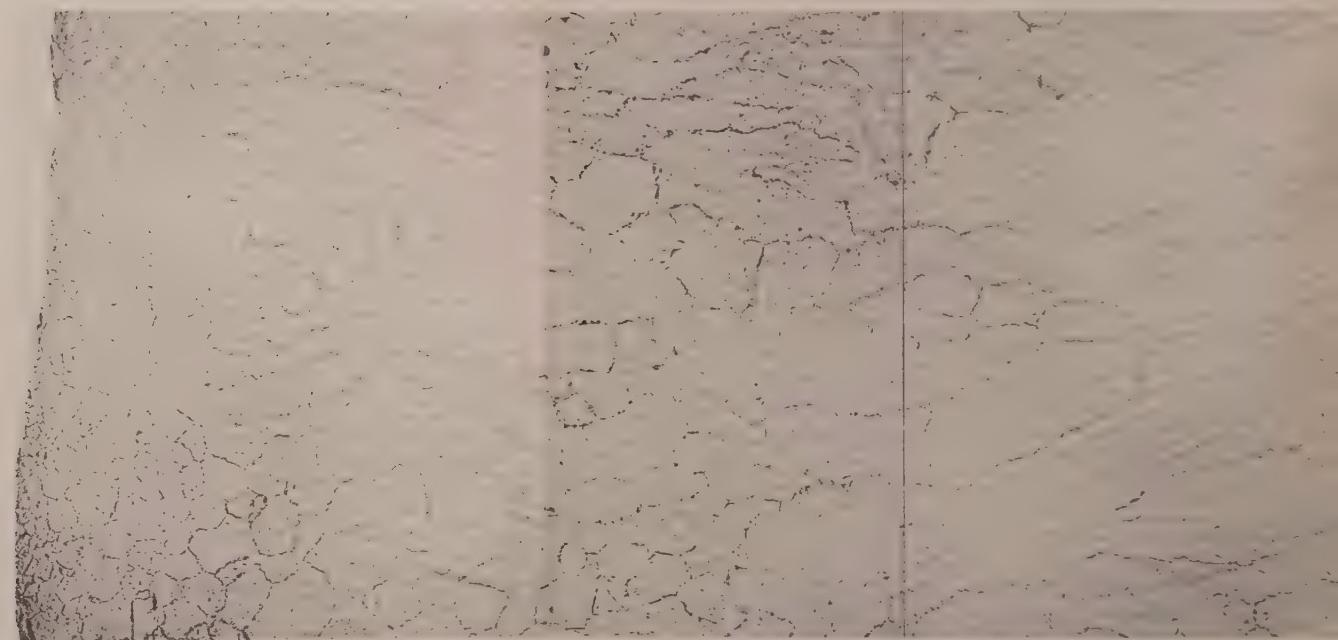


FIG. 31.—Copper Etch of Surface in Fig. 30.  $\times 15$ .



FIG. 32.—Acid Etch of Surface. Continuation of Fig. 30.  $\times 15$ .



FIG. 34.—Acid Etch of Centre of Ingot; transverse section, bottom of ingot.  $\times 15$ .

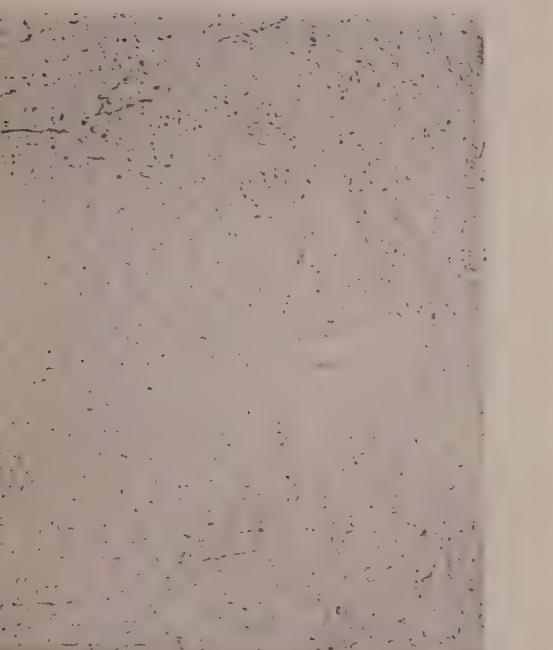


FIG. 33.—Copper Etch of Surface in Fig. 32.  $\times 15$ .

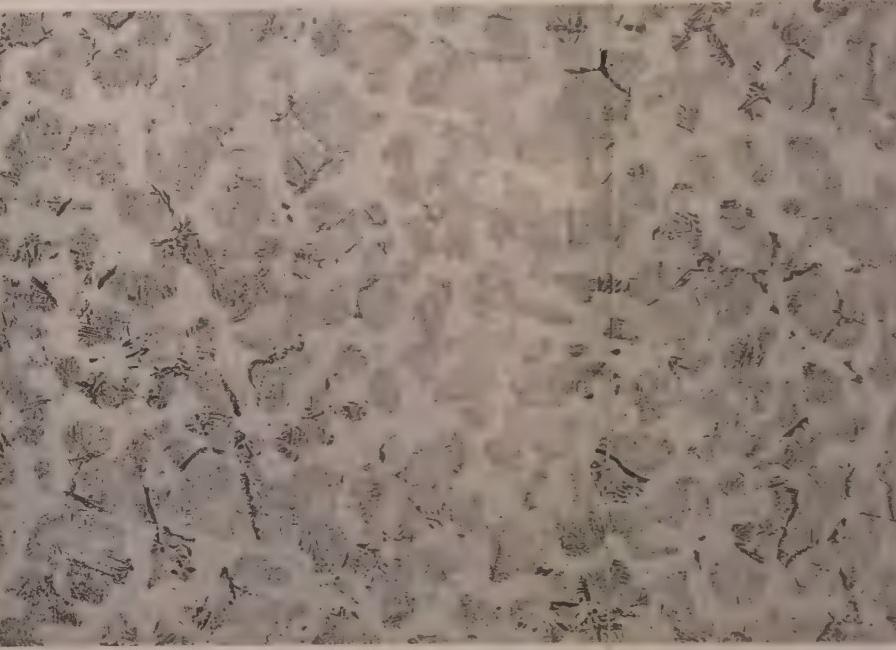


FIG. 35.—Copper Etch of Centre of Ingot in Fig. 34.  $\times 15$ .

(Illustrations reduced to four-fifths linear in reproduction.)

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FIG. 36.—Sulphur Print of Longitudinal Section at Bottom of Ingot.  $\times \frac{1}{2}$  approx.



FIG. 37.—Acid Etch of Surface in Fig. 36.  $\times \frac{1}{2}$  approx.



FIG. 39.—Portion of Sulphur Print in Fig. 41, connecting zoning with ingot structure.  $\times 3\frac{1}{2}$ .



FIG. 38.—Macro-etch of Portion of Surface in Fig. 37.  $\times \frac{1}{2}$  approx.

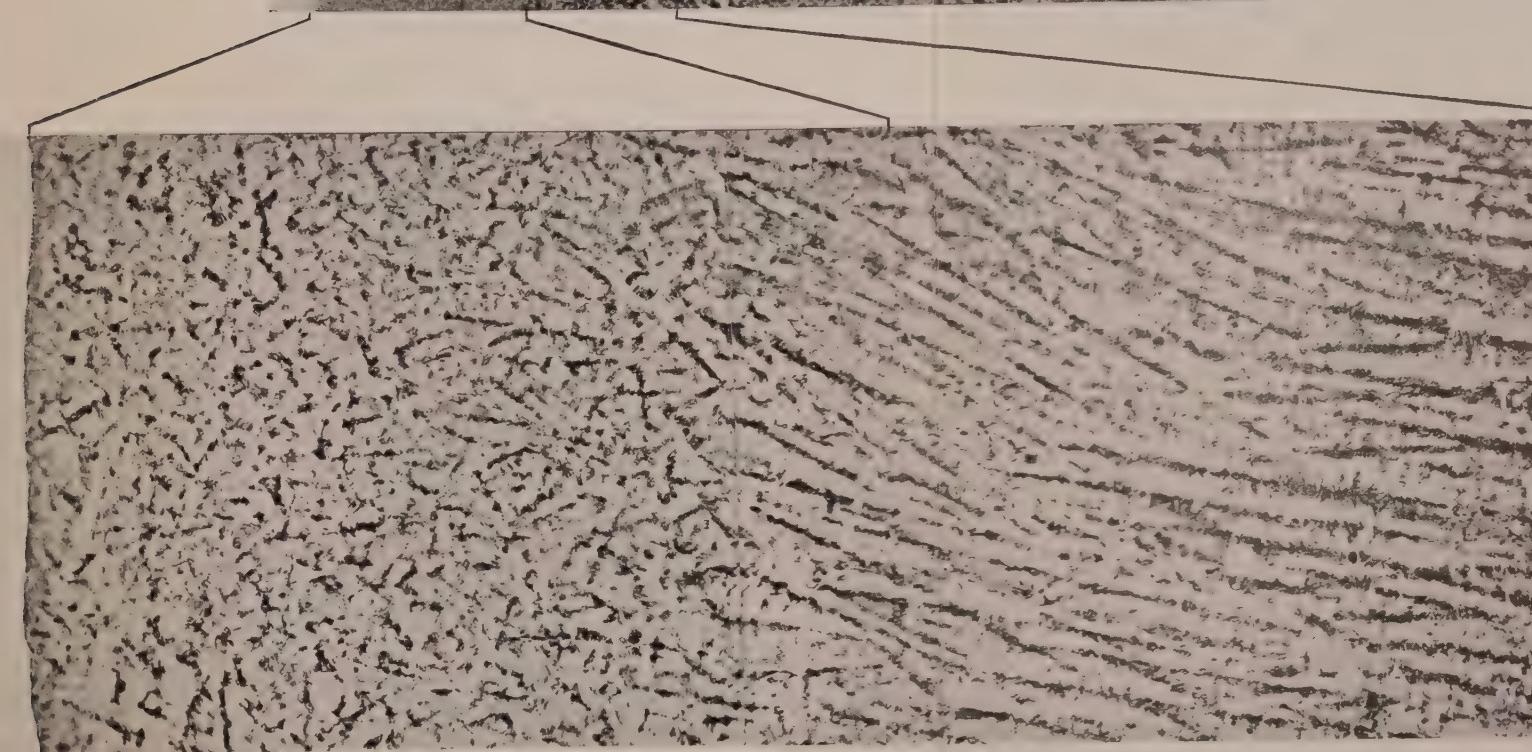


FIG. 40.—Copper Etch of Surface in Fig. 42.  $\times 15$ .

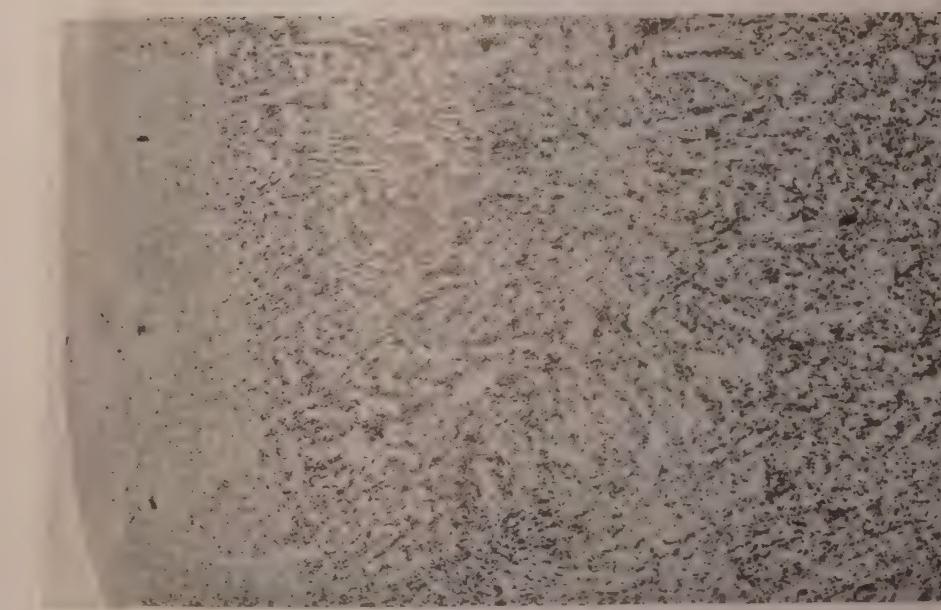


FIG. 41.—Enlargement of Portion of Sulphur Print in Fig. 36.  $\times 3\frac{1}{2}$ .

(Illustrations reduced)



FIG. 42.—Acid Etch of Surface in Fig. 36. Ingot skin on left.  $\times 15$ .

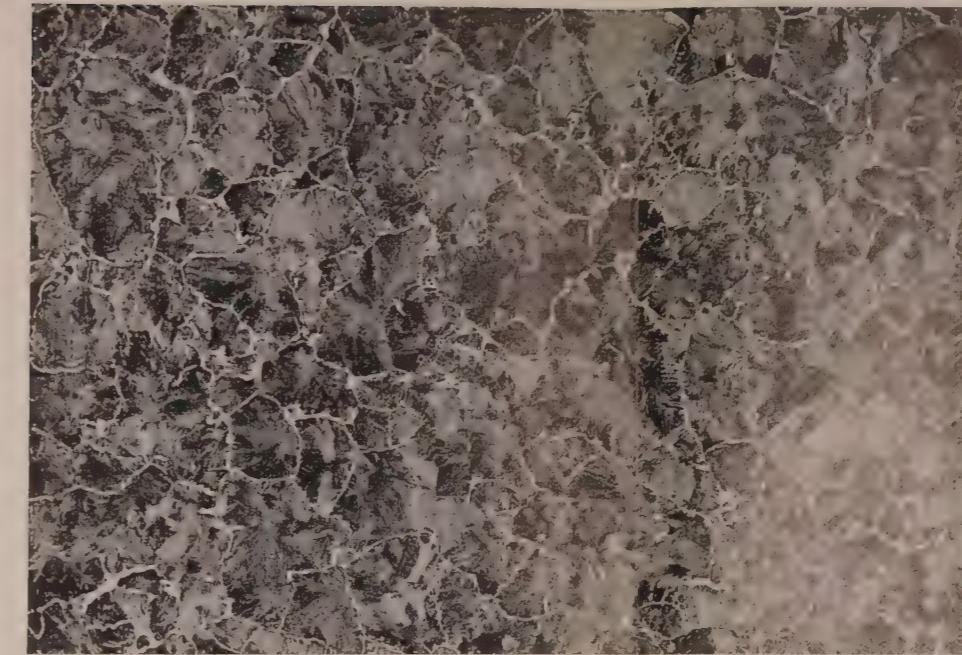


FIG. 44.—Acid Etch of Centre of Ingot, from top of longitudinal section in Fig. 36.  $\times 15$ .



FIG. 43.—Special Copper Etch to bring out Background of Grains on Surface in Fig. 42.  $\times 15$ .

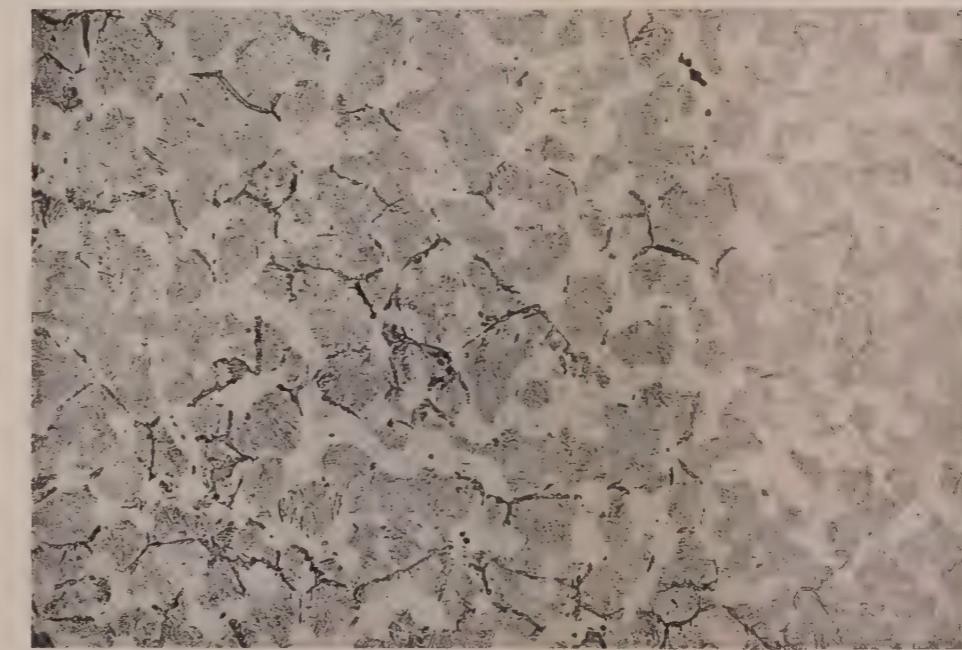


FIG. 45.—Copper Etch of Centre of Ingot in Fig. 44.  $\times 15$ .



FIG. 46.—Structure of Skin Grains of the Ingot at 9 mm. Depth in Fig. 42.  $\times 70$ .



FIG. 47.—Structure at 9 mm. Depth in Fig. 42.  $\times 70$ .



FIG. 48.—Structure at 11.5 mm. Depth in Fig. 42.  $\times 70$ .



FIG. 49.—Structure at 16 mm. Depth in Fig. 42.  $\times 70$ .



FIG. 50.—Structure at 30 mm. Depth in Fig. 42.  $\times 70$ .



FIG. 51.—Structure at the Centre of the Ingot (see Fig. 44).  $\times 70$ .



FIG. 52.—Sulphide and Silicate Inclusions at 2.5 mm. Depth in Fig. 42.  $\times 100$ .

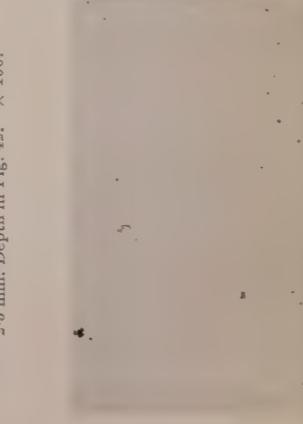


FIG. 53.—Sulphides and Silicates at 9 mm. Depth in Fig. 42.  $\times 100$ .



FIG. 54.—Inclusions at 16 mm. Depth in Fig. 42.

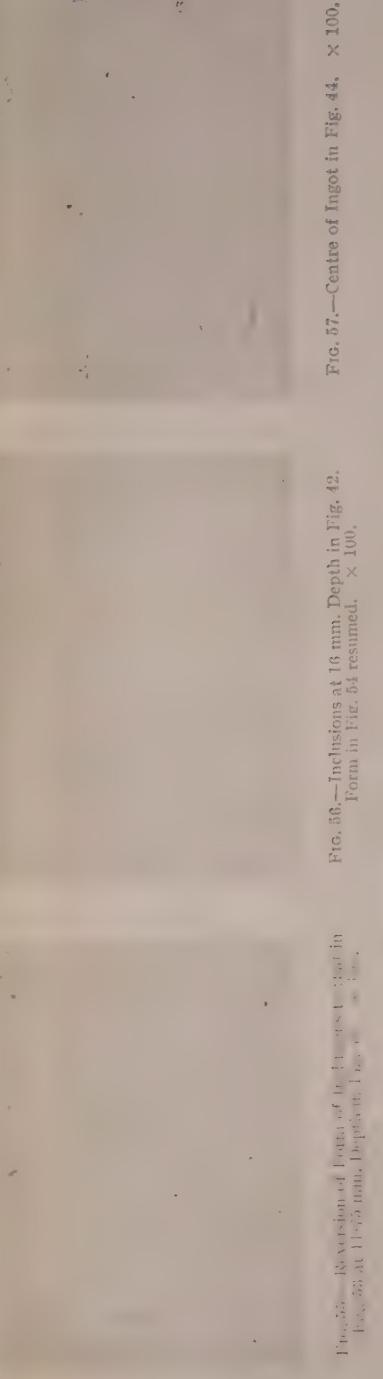
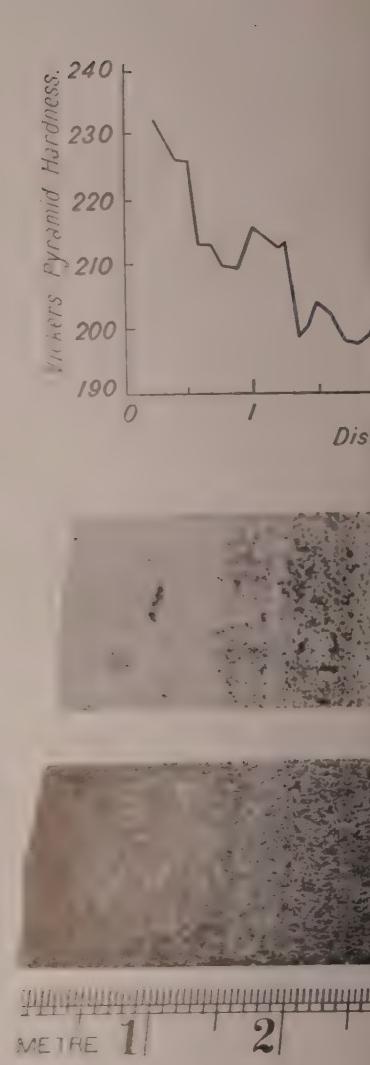
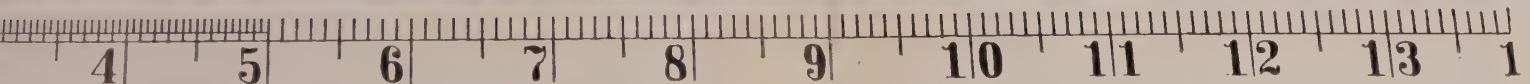
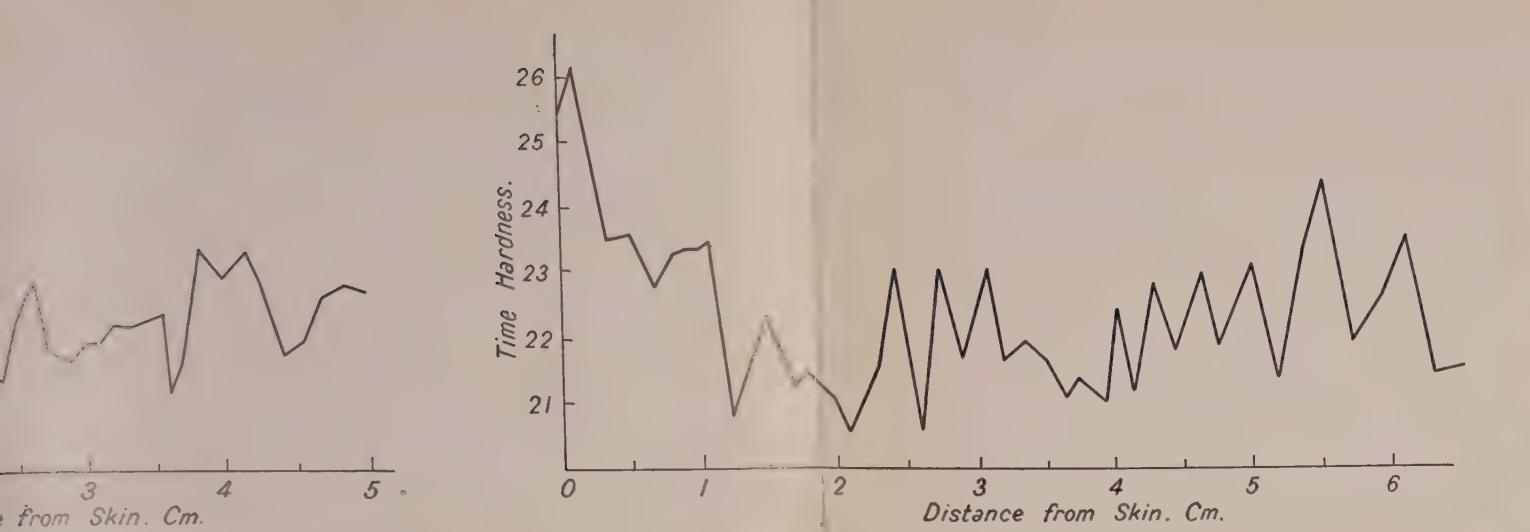


FIG. 55.—Centre of Ingot in Fig. 44.  $\times 100$ .





Print and Acid Etch of Section No. 5b<sub>2</sub>, Fig. 2 (metre rule alongside for comparison). Vickers pyramid hardness and time hardness figures also shown.



FIG. 59.—Ingot Section No. 4. Structure of metal in Fig. 32, after heat treatment at 700° C. for 1 hr. and air-cooling.  $\times 70$ .



FIG. 60.—Sulphur Print, "second print," made at Lancashire Steel Corporation, Ltd.



FIG. 61.—Sulphur Print, "first print," made at Central Research Department, The United Steel Companies, Ltd.



FIG. 62.—Macro-etch by Central Research Department, The United Steel Companies, Ltd.

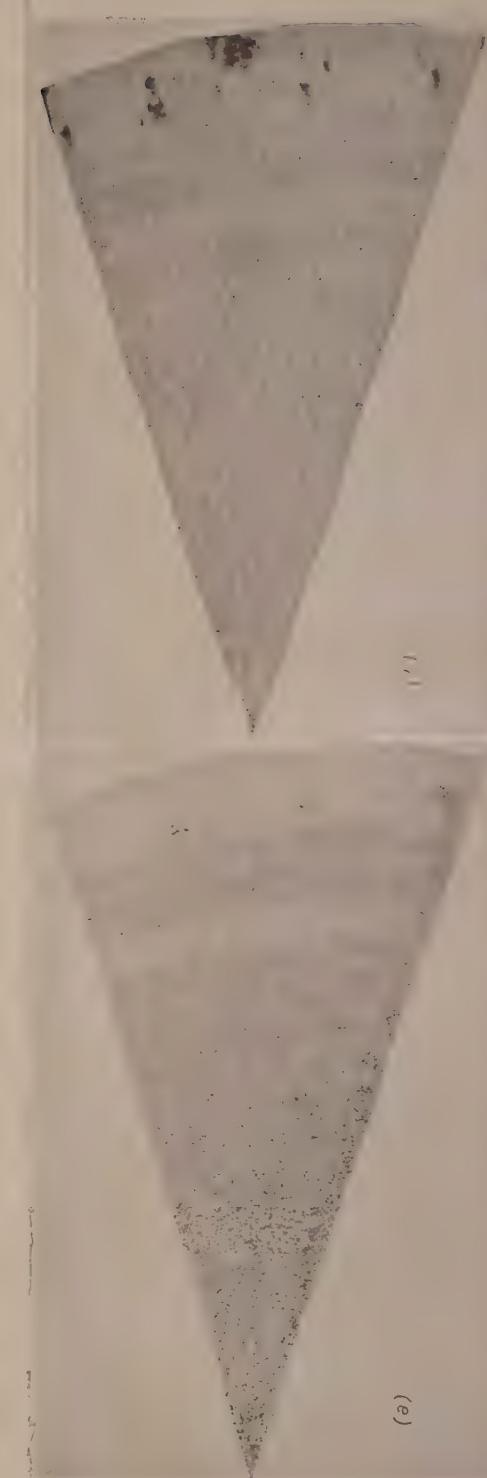


FIG. 63.—Sample Cut from Original Slice, No. 5a<sub>1</sub>. (a) (c) (d); (b) reheated at 1100° C. for 2 hr. and very slowly cooled.

From a section cut from the metal corresponding to the left-hand corner of the acid etch, Fig. 37, the following etched surfaces were prepared : An acid etch, Fig. 42; a copper etch, Fig. 40; and a copper etch to show the underlying grain contours, Fig. 43. The structural features are similar to those described in Figs. 30 and 31. The equi-axed chill crystals pass, at a depth of 0·27 in., to columnar crystals. There is not much indication of white spots until reaching the streak seen inside the columnar zone beyond a gap almost entirely free from white spots. Further in the columnar zone there is a sudden reappearance of white spots in cloud form. These white spots persist further into the metal, gradually disappearing (not photographed).

An enlarged sulphur print of adjacent metal is shown in Fig. 39 ; below, an attempt is made to correlate the sulphur-print zoning with the structural features of the metal etches.

#### *Correlation of the Sulphur Print and the Etched Surfaces.*

The junction of the first and outside light zone with the adjoining dark zone corresponds closely with the streak of white spots situated inside the columnar zone, but this coincidence might be fortuitous. Further in, the columnar zone, where the white spots abound, does not seem to mark the boundary on areas of sulphur-print zones. There is no clear and exact connection between the sulphur-print zoning and the etched surfaces, although the two might be associated.

An acid etch, Fig. 44, and a copper etch, Fig. 45, of a section cut from within  $\frac{1}{2}$  in. of the centre of the ingot show equi-axed grains. The light structure in the copper etch is duplex, again suggesting variation in concentration. These two etches, Figs. 44 and 45, were cut from positions similar to those from which Figs. 34 and 35 of section No. 4 were taken and they agree in appearance, as they should.

*Micrographs from Ingot Section No. 5.*—These were taken from the same specimen as Fig. 42, after an acid etch :

*Fig. 46.*—The structure of the skin grains at 2·5 mm. depth, showing well-developed equi-axed grains surrounding fine pearlite, also the absence of white spots of precipitated ferrite.

*Fig. 47.*—At 9·0 mm. depth from the skin. This micrograph was taken through the white streak seen in Fig. 42, i.e., inside the columnar zone.

*Fig. 48.*—At 11·5 mm. from the skin. Further in the columnar zone where the white spots are absent.

*Fig. 49.*—At 16·0 mm. from the skin; just inside the beginning of the area where white spots abound. This micrograph should be viewed at an angle of 90° to conform with the other ones.

*Fig. 50.*—At 30·0 mm. from the skin, where the white spots

are thinning out; still in the columnar-crystal zone. The form of the sulphide inclusions and the interdependence of the ferritic envelope are shown.

*Fig. 51.*—From the centre of the slice, close to the axis of the ingot, showing a normal equi-axed structure with only an occasional white spot.

*Micrographs of Non-Metallic Inclusions in Ingot Section No. 5* are shown in the following illustrations :

*Fig. 52.*—At 2·5 mm. depth from the skin. The inclusions are mainly minute sulphides and silicates. An acid etch of this area is shown in Fig. 46.

*Fig. 53.*—At 9·0 mm. from the skin. The same features appear as in Fig. 52 only slightly larger. Fig. 47 is an acid etch of this area.

*Fig. 54.*—At 11·5 mm. from the skin. Shows a change in the form of the non-metallics. An acid etch of this area is shown in Fig. 48.

*Fig. 55.*—11·75 mm. from the skin. Shows a sudden change in the form of the inclusions, reverting to the form illustrated in Fig. 53.

*Figs. 56 and 57.*—Fig. 56 is at 16·0 mm. from the skin ; this corresponds to the acid etch in Fig. 49. The eutectiform inclusions shown in Fig. 54 have been resumed, which form is retained in Fig. 57, at 30·0 mm. from the skin, and similarly right to the centre of the ingot.

In order to follow the change of structure through a longer distance, a specimen 14 cm. long was cut from an ingot slice adjacent to section No. 5 ; the specimen was taken from the bottom of the ingot where it rounded off, and was cut normal to the surface into the steel, see Fig. 2, section 5b<sub>2</sub>. Fig. 58 shows an acid etch on this specimen (lower portion) and the sulphur print from the reverse side of the same specimen,  $\frac{3}{4}$  in. thick (upper portion). A centimetre scale has been laid alongside the specimen from which distances can be measured. The following features are observable :

*Acid Etch.*—The structure of the skin crystals is equi-axed and extends to a depth of 1·3 or 1·4 cm. At a depth of 1·5 cm. the surface is lighter in tint, owing to the cloud precipitation of white spots of ferrite. These white spots gradually thin out, and beyond a depth of 6 or 7 cm. they are sensibly absent.

The columnar crystals extend from a depth of 1·3–1·4 cm. to about 4·5 cm., where the structure becomes equi-axed, which condition is maintained to the centre of the ingot.

*Sulphur Print.*—This shows clearly the zoning already mentioned, but there is no obvious connection between the zoning on the sulphur print and structural changes seen on the acid etch.

### *Hardness Determinations.*

Vickers pyramid hardness determinations over the first 5 cm. have been graphed in Fig. 58; the hardness falls to a minimum at a distance inwards of 1.75 cm.

Time hardness determinations, obtained by the Herbert pendulum hardness tester, also show a similar minimum.

### THE DISTRIBUTION AND INTENSITY OF THE WHITE SPOTS OF PRECIPITATED FERRITE.

The following comments on the distribution and intensity of the white spots of precipitated ferrite in the ingot sections may be made :

*Ingot Section No. 1.*—Feeder head. The white spots are almost entirely, if not completely, absent.

*Ingot Section No. 2.*—The white spots are present from the skin of the ingot inwards, although not as a dense cloud. They are, perhaps, a little more numerous in the columnar zone, but since they are thinning out on passing into the ingot their association with the columnar zone is fortuitous. They gradually thin out, but are still present on the left side of Fig. 14. They are present only occasionally over the remainder of Fig. 14 and will probably retain this occasional distribution far into the ingot.

*Ingot Section No. 3.*—The white spots form a dense cloud from the skin and throughout Fig. 22. They are still fairly dense over the first third of the second acid etch, Fig. 24, although not quite so numerous as in Fig. 22. They then suddenly disappear almost completely before the termination of the columnar zone. This sudden disappearance over the last crystal length of the columnar zone is followed by a light distribution in the equi-axed zone, which distribution extends further into the ingot.

*Ingot Section No. 4.*—The first real presence of white spots is at just about the commencement of the columnar zone, where a narrow belt or streak is seen running parallel to the surface just less than half-way along Fig. 30 from the ingot skin, 0.30 in. from the surface at the top of the specimen and 0.33 in. at the lower end. At a distance of 0.53 in. inwards from the surface and well inside the columnar zone the spots appear as a dense cloud, which cloud gradually thins out but is still present at the inside of Fig. 32, where the equi-axed zone commences. Further in the ingot the spots are still present in attenuated distribution in the equi-axed zone.

*Ingot Section No. 5.*—Fig. 42 corresponds closely in ingot position to section No. 4, and the remarks made on that section generally apply here, except that the belt or streak of white

spots, 0·37 in. in from the surface, is now well inside the columnar zone.

There is no exact connection between the position of the white spots and the crystal structure of the ingot. However, they are not present, at least to any extent, in the surface equi-axed chill zone, which zone is only present to any extent in the bottom half of the ingot.

The following are the depths of the equi-axed chill crystals and columnar crystals in ingot sections Nos. 2 to 5 :

Section No.	Depth of Equi-axed Chill Crystals.	Depth of Columnar Crystals.
2	Unappreciable	0·43 in.
3	0·03 in.	1·57 in.
4	0·33 in.	1·80 in.
5	0·27 in.	1·73 in.

The white spots can be seen from Figs. 47, 49 and 50 to be made up of a precipitation of ferrite on a non-metallic inclusion of silicate or sulphide.

A specimen already examined, Fig. 32, was heated to 720° C. for 1½ hr. and cooled in air. Fig. 59 shows the structure produced. The white spots have all disappeared and the grains have been recrystallised, leaving no trace of an as-cast structure.

#### MICROSTRUCTURE OF THE CENTRE OF THE INGOT.

The absence of massive ferrite boundaries due to carbon segregation in the high position in the ingot occupied by section No. 2 is the only real difference between the microstructure of this section (Fig. 16) and those of sections Nos. 3, 4 and 5 (Figs. 26, 34 and 44), which are similar in general appearance.

#### EFFECT OF HEAT TREATMENT ON SULPHUR-PRINT ZONING.

A section from the bottom of the ingot was heated to 1150° C. for 1½ hr. and cooled in the furnace. A sulphur print from this heat-treated piece still showed zoning, with no positive indication of change in intensity of the individual zones concerned.

However, further tests are in hand to explore the effect of heat on the zones at other temperatures and for different periods of heating.

#### DETAILED ANALYSIS OF ZONED AREAS AS REVEALED BY A SULPHUR PRINT.

Two slices, Nos. 5a and 5b in Fig. 2, each about 1 in. thick, were cut from the bottom of the ingot, from a position adjacent to the slice sulphur-printed and reproduced in Fig. 36. The sulphur-print zoning was similar to that shown in Figs. 28 and 36.

*Examination made at Lancashire Steel Corporation, Ltd.*

From a straight length of 7 in. at the bottom of section No. 5b millings,  $\frac{1}{32}$  in. at a time, were cut from the surface right through the various zones and were analysed for carbon, sulphur, phosphorus and manganese. Silicon was also determined on mixed samples of the remaining millings, a few samples at a time.

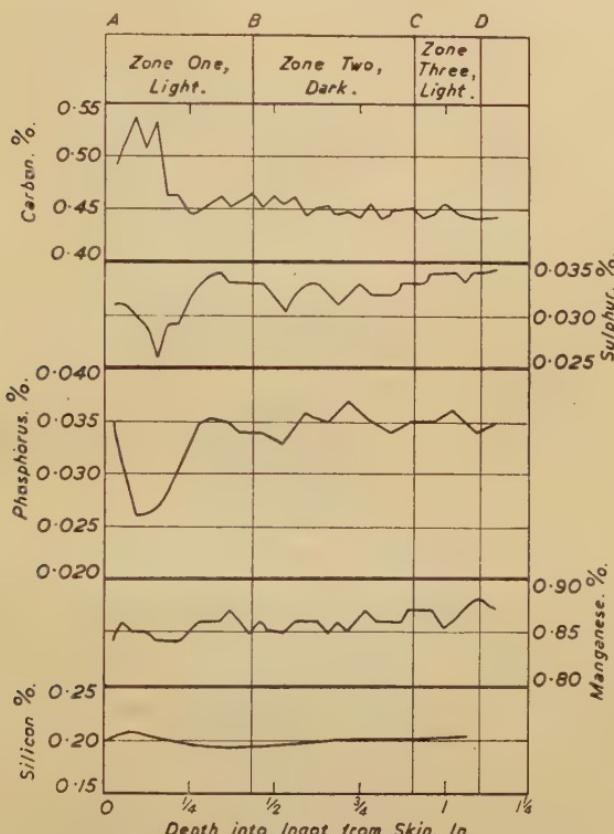


FIG. 64.—Analysis of Metal from the Skin and through the Zoned Area of Section No. 5b, Fig. 2.

All the analyses are recorded in Table III., and are graphed in Fig. 64.

Check sulphur prints were taken after every few cuts to enable a correlation to be made between the analysis and the position in the zoning.

It will be seen in Table III. that there is an increase in carbon over the first five cuts, to a depth of  $\frac{5}{32}$  in., followed by a carbon value of 0.46%, which after twenty cuts falls to 0.45%.

TABLE III.—*Shell-Steel Ingot. Analyses of Millings from Ingot Section 5b<sub>1</sub>.*

Cut No.	C. %.	S. %.	P. %.	Mn. %.	Cut No.	C. %.	S. %.	P. %.	Mn. %.
<i>Separate Lots of Millings.</i>									
1	0.490	0.031	0.035	0.84	20	0.450	0.033	...	0.86
2	0.513	0.031	...	0.86	21	0.454	0.032	0.035	0.85
3	0.538	0.030	0.026	0.85	22	0.447	0.031	...	0.86
4	0.507	0.029	...	0.85	23	0.448	0.032	0.037	0.85
5	0.534	0.026	0.0265	0.84	24	0.443	0.033	...	0.86
6	0.462	0.029	...	0.84	25	0.456	0.032	0.035	0.87
7	0.462	0.029	0.0305	0.84	26	0.442	0.032	...	0.86
8	0.446	0.032	...	0.85	27	0.449	0.032	0.034	0.86
9	0.448	0.033	0.035	0.86	28	0.450	0.033	...	0.86
10	0.455	0.034	...	0.86	29	0.452	0.033	0.035	0.87
11	0.462	0.034	0.035	0.86	30	0.443	0.033	...	0.87
12	0.452	0.033	...	0.87	31	0.446	0.034	0.035	0.87
13	0.459	0.033	0.034	0.86	32	0.455	0.034	...	0.85
14	0.464	0.033	...	0.85	33	0.448	0.034	0.036	0.86
15	0.451	0.033	0.034	0.86	34	0.444	0.033	...	0.87
16	0.463	0.032	...	0.85	35	0.444	0.034	0.034	0.88
17	0.455	0.030	0.033	0.85	36	0.444	0.034	...	0.88
18	0.464	0.032	...	0.86	37	0.443	0.034	0.035	0.87
19	0.444	0.033	0.036	0.86					
Cuts Nos.		Si. %.	Cuts Nos.		Si. %.	Cuts Nos.		Si. %.	
<i>Mixed Millings.</i>									
1, 2 & 4 6-11	0.208 0.198		12-18 19-25		0.196 0.202		26-31 32-37		0.202 0.202

Sulphur and phosphorus behave inversely to the carbon in that they fall to a minimum at a depth of five cuts, and then rise to a figure in keeping with the pit analysis.

Manganese is steady, except, perhaps, the first few readings, at a figure 0.01-0.02% lower than the pit figure.

Silicon was not determined so extensively as the other elements, but appears to be steady at about the pit figure.

*Examination made at Central Research Department, The United Steel Companies, Ltd.—Contribution from T. Swinden, D.Met.*

From the other, adjacent, slice, No. 5a, a similar portion, No. 5a<sub>1</sub>, was cut, and was sent to the Central Research Department, The United Steel Companies, Ltd., for examination, by permission of Dr. Swinden, Director of Research, whom the author thanks for his kindness in so willingly arranging for this work to be done. An account of this examination, furnished by Dr. Swinden, follows :

This section, No. 5a<sub>1</sub>, had been sulphur-printed at the Lancashire Steel Corporation before despatch, and a reproduction of their sulphur print is shown as Fig. 60. At least four clearly marked

zones are apparent, but it must be pointed out that this print is a "second print," obtained immediately following a "first" print on the same polished surface. We were informed that this zoning is not shown so clearly on the "first" print, and normal sulphur-printing carried out in C.R.D. confirms this statement. In the "first" sulphur print at C.R.D. (see Fig. 61) the zoning is not so marked as in Dr. Binnie's "second" print, and in the macro-etch (by C.R.D.) shown in Fig. 62, little evidence of the zoning can be seen.

### *Chemical and Metallurgical Examination.*

In view of the difficulty in reproducing the clearly marked zoning by normal sulphur-printing methods, it was decided to explore the variations of sulphur content from the outside to a point well beyond the various zones, by both chemical and microscopical means, in addition to the oxygen determinations on the four main zones as requested by Dr. Binnie.

(1) *Chemical Examination of Sulphur Variation.*—A strip,  $1\frac{3}{8}$  in. in width, was cut from the section and millings were taken by successive cuts of  $\frac{1}{16}$  in. from the outer edge to a depth of  $1\frac{1}{2}$  in. There were 24 samples in all, extending definitely into the fourth zone. On many of these samples sulphur determinations were made by both the gravimetric and combustion methods.

The sulphur determinations were checked subsequently on drilled samples, representing, so far as possible, the main bulk of the four zones.

(2) *Vacuum Fusion Determinations of Oxygen Content.*—These were carried out on specimens cut from each of the four different areas shown by the sulphur prints. In view of the high manganese content of this steel, repeat determinations were made by the tin-alloy method, designed to overcome the deleterious effect of high manganese in the vacuum fusion method for oxygen in steel.

(3) *Microscopical Examination.*—Microscopical examination was carried out on a piece  $1\frac{1}{2}$  in.  $\times \frac{1}{2}$  in., extending from the outside to a point well inside the centre zone. Comparative inclusion counts were made of the oxide and sulphide inclusions occurring in two directions, parallel to, and across, each zone.

Fig. 65 shows in diagrammatic form the positions of the various test samples described above.

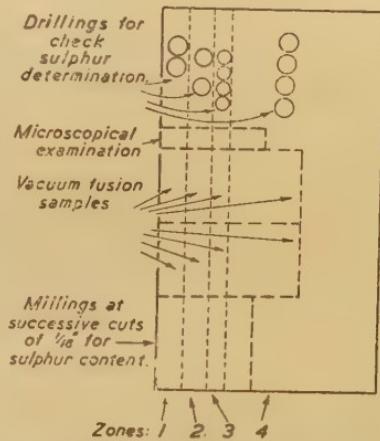


FIG. 65.—Positions of Test Samples in Ingot Section No. 5a<sub>1</sub>.

*Results of the Examination.*

Table IV. gives the results of sulphur determinations by chemical analysis.

The oxygen contents by vacuum fusion are recorded in Table V.

TABLE IV.—*Sulphur Determinations at Specified Positions in Ingot Section No. 5a<sub>1</sub>.*

Successive cuts of  $\frac{1}{16}$  in.

Width of Zone.	No. of Sample of $\frac{1}{16}$ in. Depth.	Sulphur. %.	Mean Sulphur of Zone. %.	Sulphur Content of Drilled Samples. %.
No. 1. 10 mm. (Outside).	1	0.030	0.032	0.030
	2	0.029		
	3	0.033		
	4	0.031		
	5	0.034		
	6	0.034		
	7	0.033		
Junction	8	0.033	0.032 <sub>5</sub>	0.033
	9	0.034		
	10	0.032		
	11	0.033		
	12	0.032		
	13	0.032		
	14	0.030		
No. 3. 7 mm.	15	0.031	0.031	0.031
	16	0.031		
	17	0.033		
	18	0.034		
No. 4.	19	0.033	0.032	0.034
	20	0.034		
	21	0.030		
	22	0.032		
	23	0.030		
	24	0.032		

TABLE V.—*Oxygen Contents by Vacuum Fusion of Specified Zones in Ingot Section No. 5a<sub>1</sub>.*

Zone.	Oxygen. %.	Nitrogen. %.
No. 1 (Outside)	0.011	0.003 <sub>5</sub>
No. 2	0.007 <sub>5</sub>	0.004 <sub>0</sub>
No. 3	0.007	0.003 <sub>5</sub>
No. 4	0.005 <sub>5</sub>	0.004

Table VI. contains the comparative inclusion counts of the four zones.

TABLE VI.—*Comparative Inclusion Counts of Specified Zones in Ingot Section No. 5a<sub>1</sub>.*

Zone.	Width of Zone. Mm.	Along Centre of each Zone and at Right Angles to Surface of Section.		At Right Angles to Direction of Zoning and Parallel to Surface of Section.		Mean Value per Field examined.	
		Average Value per Field examined.					
		Oxides.	Sulphides.	Oxides.	Sulphides.	Oxides.	Sulphides.
No. 1	10	3.6	3.5	7.0	3.2	5.3	3.4
No. 2	10	2.5	6.0	4.5	8.9	3.5	7.5
No. 3	7	1.5	3.0	2.9	2.7	2.2	2.9
No. 4	...	1.5	5.0	2.7	9.5	2.1	7.3

NOTE :—The first counts were made on an equal number of fields, *i.e.*, 22, but, owing to the varied width of the zones, the number of fields in each zone for the second count was not uniform. Hence, the results for both counts are given on the basis of inclusions per field. The effect of varying size of the inclusions in the index figures is included in the evaluation.

#### Comments.

(1) Zoning in the sulphur prints observed by Dr. Binnie is confirmed, but the "second" (and subsequent) prints show this much more clearly than the "first" print. The explanation may be found in the technique of printing, but such modifications as have been tried have not succeeded in producing such marked contrasts in the first as in subsequent prints. Macro-etching is still less effective in revealing zoning.

(2) Chemical determination of sulphur in the respective zones shows only minor differences—far less than might have been expected from the appearance of the sulphur prints. This is important, indicating apparently a difference in the response of the sulphides to acid attack, and, by inference, a difference in the state of existence of the sulphides in the respective zones.

(3) The vacuum fusion determinations show a decreasing oxygen content in each successive zone and also a uniform nitrogen content. This is in line with our usual experience; the first zone, being a chill zone, corresponds in oxygen content to the ladle metal; the subsequent zones tend to be lower in oxygen, owing to preferential freezing of purer metal during the longer period of cooling.

(4) The quantitative inclusion counts for oxides and sulphides are noteworthy. The decreasing oxides content is in line with the oxygen determinations, but the sulphides give striking confirmation of the sulphide differences revealed in the sulphur prints.

(5) Thus, the microscopical evidence, as regards sulphur content, is at variance with the chemical examination. No satisfactory explanation is immediately available, and, as far as we are aware, no direct quantitative correlation between sulphide inclusions

measured microscopically and sulphur content by chemical analysis has yet been fully established.

However, it may be noted that the total sulphur content in steel, as determined chemically, includes not only the visible sulphides occurring as a separate phase, but also soluble sulphide constituents.

*Supplementary Note by Dr. T. Swinden.*

Two small pieces of additional work have been done on the samples received from Dr. Binnie.

*Carbon Content of the Respective Zones.*—Drillings representative of each zone were taken from the section as received and careful carbon determinations carried out, with the following results :

	Carbon.
(1) Outer chill zone (of apparent low sulphur content) . . . . .	0·47%
(2) Inner zone (of apparent high sulphur content) . . . . .	0·44%
(3) Inner zone (of apparent lower sulphur content) . . . . .	0·45%
(4) Main inner zone . . . . .	0·455%

There is thus no important carbon variation corresponding to the respective zones revealed on sulphur-printing.

*The Effect of Reheating.*—A sample was cut from the original slice and was soaked at 1100° C. for 2 hr. followed by slow cooling at the rate of 10° per hr. On subsequently sulphur-printing, it was found that the treatment has not removed the zoning effect. This is illustrated in Fig. 63, which incidentally represents "second" sulphur prints of both specimens.

*Interpretation of "First" and "Second" Sulphur Prints.*

The question of the interpretation of "first" and "second" sulphur prints arises from Dr. Swinden's contribution. Whilst the "second" sulphur print showed a heavier contrast in the definition of the zones, nevertheless the zones were still well defined on the "first" print. This is seen by reference to the sulphur prints reproduced throughout the paper, all of which, e.g., Figs. 28, 36, 58, &c., were "first" prints, with the sole exception of Fig. 3, the sulphur print of the ingot, which was selected for reproduction in preference to the "first" print on account of the sharper overall resolution in the dendritic structures. This "first" print of the ingot also showed clearly defined zoning and was, of course, the original indication that zoning was present.

CLOSING REMARKS AND ACKNOWLEDGMENTS.

An investigation into the structure and features of a whole ingot opens up very many problems, each one of which is a study in itself, and the author would prefer to leave further detailed research until a later date, otherwise publication of the facts so far revealed from the examination of the ingot would be held up unduly.

The author wishes to thank Mr. J. Sinclair Kerr, Assistant Managing Director of the Lancashire Steel Corporation, Ltd., not only for permission to carry out this work and to publish the results but also for his interest throughout; also the staff of the laboratories, especially Mr. J. C. Booth for the sulphur-printing and the photographic work, Mr. J. Harrison for the chemical analyses and Mr. W. A. Jenks for the sulphur print of the ingot and general control over the cutting of the ingot.

The collaboration of the Open-Hearth and Engineering Departments in this work is acknowledged.

Dr. Swinden's valuable contribution extends the scope of the paper and the author's thanks to him are recorded.

[This paper was discussed jointly with the following one by T. Swinden on "The Examination of a Rimming-Steel Ingot Containing 0·29% of Carbon."]



# THE EXAMINATION OF A RIMMING-STEEL INGOT CONTAINING 0·29% OF CARBON.<sup>1</sup>

By T. SWINDEN, D.MET. (DIRECTOR OF RESEARCH, CENTRAL RESEARCH DEPARTMENT, THE UNITED STEEL COMPANIES, LTD., STOCKSBURGE, NEAR SHEFFIELD).

(Figs. 2 and 3 = Plate XXXIII.)

*Paper No. 27/1944 of the Committee on the Heterogeneity of Steel Ingots.*

## SUMMARY.

A 2½-ton ingot of rimming steel containing 0·29% of carbon was examined with particular reference to carbon distribution. There were significant differences in the behaviour of this steel as compared with low-carbon rimming steel during solidification, but nevertheless the heterogeneity was of the same general character. The rim contained about 0·25% of carbon, and, in answer to previous suggestions on the point, it is submitted that this could not have been deposited as primary crystals of δ-iron.

## *Introduction.*

IT has been repeatedly suggested that the occurrence of a relatively pure rim zone in low-carbon rimming steel may be due to the primary precipitation of iron in the δ form. The hypothesis has never been elaborated, but presumably it might be suggested that the mechanism of solidification would be somewhat along the following lines :

The carbon monoxide evolution on the advancing rim wall, resulting from the carbon and oxygen reaction during effervescence, continuously sweeps away the mother-liquor (which is being gradually enriched in carbon and oxygen), thereby acting as a barrier between precipitated δ-iron and the mother-liquor. The peritectic transformation, *i.e.*, the reaction between δ-iron and mother-liquor, is thereby suppressed, and the rim solidifies with a lower content of carbon—and other constituents—than when solidification occurs in the quiescent manner of killed solid steels. Since most commercial rimming steels are cast from a liquid metal having a carbon content below about 0·2%, the formation of a rim zone with a carbon content of approximately 0·1%, which is the limit for δ-iron according to Adcock's diagram, affords a basis for this hypothesis.

<sup>1</sup> Received February 1, 1944. This paper is published by authority of the Committee on the Heterogeneity of Steel Ingots. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

One difficulty in accepting this theory, in the author's mind, has always been the profound effect of a small addition of silicon or aluminium, which, as is well known, is capable of completely suppressing the rimming action. It is difficult to fit this fact into the δ-iron theory.

However, the question arose again in the Ingots Committee as to what the carbon content would be if a steel containing considerably over 0·2% of carbon was produced as a rimming quality. Mr. James Mitchell, of Messrs. Stewarts and Lloyds, Ltd., kindly undertook to provide a typical ingot of this grade, and the present note is the result of a joint examination with Mr. Mitchell, to whom the author tenders his best thanks for most helpful collaboration, of a basic open-hearth ingot, of which the pit sample contained 0·29% of carbon. A typical analysis would be :

Manganese.	Silicon.	Sulphur.	Phosphorus.
0·4%	Trace.	0·025%	0·025%

The selected ingot was approximately 20 in. square and weighed  $2\frac{1}{2}$  tons.

Certain striking differences in the rimming process are noted between this type of material and low-carbon rimming steel. The effervescence itself is more akin to an ebullition similar to the "boil" of a bath of steel in the furnace; in other words, the gas evolution is in relatively large bubbles from a relatively small number of points per unit volume, as compared with the indefinitely large number of small bubbles that one gets during the effervescence of low-carbon steel. Another point is that this type of steel invariably produces a thick viscous scum on the top of the ingot during effervescence instead of the usual fluid slag which rises in low-carbon basic Bessemer material. It is also almost invariably found necessary to plate these ingots towards the end of the so-called effervescence to avoid final eruption which gives a volcano top.

It will be seen from the report which follows that the sharp demarcation between the rim and core, common to low-carbon rimming steels, is replaced in this case by an indeterminate zone of approximately 1-in. depth, but nevertheless the heterogeneity of this ingot is of the same general character as that of a low-carbon rimming steel.

#### *Scheme of Investigation.*

Two adjacent strips ( $1\frac{3}{8}$  in.  $\times \frac{7}{8}$  in.  $\times 10$  in.), from outside to centre, were cut from the ingot at its mid-height. One strip was examined by Mr. Mitchell for variation in the carbon content of successive samples, each representing a depth of  $\frac{1}{4}$  in.; on the other strip, sulphur-printing and macro-examination, followed by check carbon determinations at the extreme edge and oxygen determinations at selected positions, were carried out in the author's laboratories.

The carbon results obtained by Mr. Mitchell are given in Table I. and shown graphically in Fig. 1. In order to examine more closely the carbon content of the extreme edge, additional carbon analyses were made by the author on the adjacent slice. These results, shown in Table II., correspond to depths of  $\frac{1}{16}$  in.,  $\frac{1}{8}$  in. and  $\frac{3}{16}$  in., respectively, from the outer surface of the ingot, thus representing a total depth slightly greater than the first sample analysed by

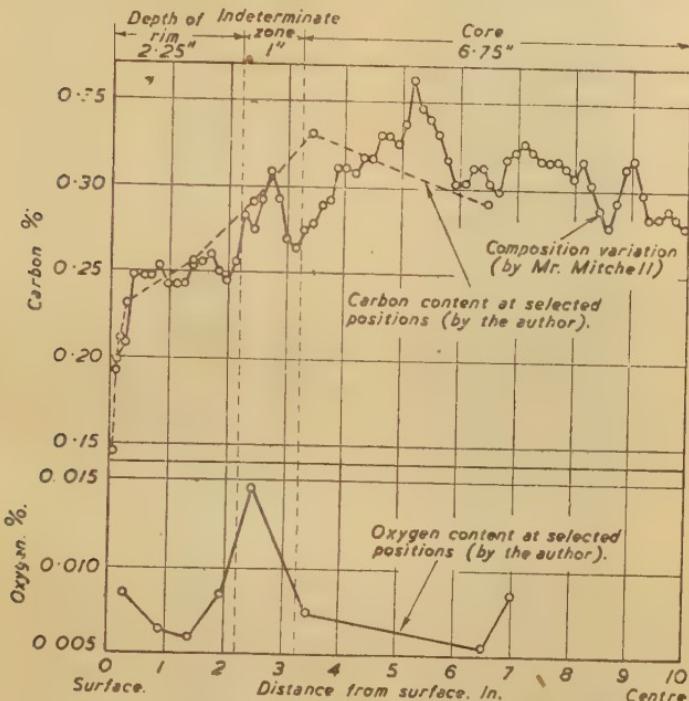


FIG. 1.—Variation of Carbon and Oxygen Contents from Outside to Centre of a 0.29% Carbon Rimming-Steel Ingot.

Mr. Mitchell. The effect of this more detailed sampling is to show an even lower carbon content at the extreme edge and a rapid increase in the second and third samples to values similar to that of the first sample reported by Mr. Mitchell. These additional carbon results are also given in Fig. 1.

The results of oxygen determinations, by the vacuum fusion method, at selected positions along the second slice are given in Table III., together with carbon determinations carried out on the surplus material removed during the machining of the vacuum fusion specimens. The carbon and oxygen values given in Table III. represent the contents of these elements in an area of sample  $\frac{1}{2}$  in. square.

TABLE I.—*Carbon Contents at Successive Positions from Outside to Centre.*

By Mr. Mitchell.

Sample No.*	Carbon. %.	Sample No.*	Carbon. %.	Sample No.*	Carbon. %.
1 (outside)	0·197	24	0·277	47	0·315
2	0·207	25	0·287	48	0·320
3	0·246	26	0·291	49	0·324
4	0·246	27	0·310	50	0·320
5	0·246	28	0·310	51	0·315
6	0·252	29	0·306	52	0·315
7	0·242	30	0·315	53	0·315
8	0·240	31	0·315	54	0·310
9	0·242	32	0·329	55	0·305
10	0·252	33	0·329	56	0·315
11	0·254	34	0·324	57	0·301
12	0·258	35	0·334	58	0·287
13	0·249	36	0·362	59	0·277
14	0·244	37	0·343	60	0·291
15	0·254	38	0·338	61	0·310
16	0·282	39	0·329	62	0·315
17	0·273	40	0·315	63	0·296
18	0·291	41	0·301	64	0·282
19	0·306	42	0·301	65	0·282
20	0·291	43	0·310	66	0·287
21	0·268	44	0·310	67	0·282
22	0·263	45	0·301	68 (centre)	0·277
23	0·273	46	0·296		

\* In steps of  $\frac{1}{16}$  in. from outside to centre.*Metallurgical Examination.*

The sulphur print (Fig. 2) shows the occurrence of an indefinite zone between the rim and core, commencing at a depth of  $2\frac{1}{4}$  in. and extending inwards for approximately 1 in. The rim zone was not as pure nor was the core as heavily segregated as a normal

TABLE II.—*Carbon Contents of Outer Skin.*

By the author.

Sample No.	Distance from Outer Surface. In.	Carbon. %.	
		O.R.D.	S. & L.
1 (C.R.D.)	$\frac{1}{16}$	0·14 <sub>5</sub>	...
2 (C.R.D.)	$\frac{1}{8}$	0·19	...
1 (S. & L.)	$\frac{1}{7}$	...	0·197
3 (C.R.D.)	$\frac{3}{16}$	0·21	...
2 (S. & L.)	$\frac{2}{7}$	...	0·207

rimming-steel section. Slight evidence of an  $\Lambda$ -segregate approximately  $5\frac{3}{4}$  in. from the outer surface of the ingot was apparent, but there was no central segregation.



FIG. 2.—Sulphur Print.



FIG. 3.—Macro-Etch.

Figs. 2 and 3.—0·29% Carbon Running-Steel Ingot; strip from outside to centre.



The macroscopic etching (Fig. 3) reveals the presence of three zones :

(1) An outer chilled zone, approximately  $\frac{1}{4}$  in. in width, of small crystals.

(2) A zone,  $1\frac{3}{4}$  in. in width, of columnar crystals, containing also a number of small lenticular-shaped blow-holes.

(3) An inner zone of equi-axed crystals, 8 in. in width, showing at the indeterminate zone coarse crystals which were markedly refined towards the centre of the ingot. Near the indeterminate rim-core junction large irregular blow-holes were present, extending over a depth of from  $1\frac{3}{4}$  in. to  $4\frac{3}{4}$  in. from the outer surface of the ingot. The central area of the ingot slice was comparatively sound.

TABLE III.—*Oxygen and Carbon Contents at Selected Points.*

By the author.

Sample No.	Distance of Mid-Point of Sample from Outside. In.	Position in Slice.	Oxygen. %.	Carbon. %.
1	$\frac{1}{4}$	Rim.	0·008 <sub>5</sub>	0·23
1A	$\frac{7}{8}$	"	0·006 <sub>5</sub>	...
2	$1\frac{3}{8}$	"	0·006	0·25 <sub>5</sub>
2A	$1\frac{15}{16}$	"	0·008 <sub>5</sub>	...
3	$2\frac{7}{16}$	Indeterminate zone.	0·014 <sub>5</sub>	0·29
4	$3\frac{7}{16}$	Core.	0·007 <sub>5</sub>	0·33
5	$6\frac{1}{2}$	"	0·005 <sub>5</sub>	0·29
5A	7	"	0·008 <sub>5</sub>	...

#### *Chemical Examination.*

The carbon and oxygen analyses show a composition variation different in some characteristics from that of a normal rimming steel. The outer edge of the ingot has the very low carbon content of 0·14<sub>5</sub>% that increases rapidly to 0·25%, which is the average figure over the major part of the rim zone. The indeterminate zone shows a minor peak at 0·30<sub>5</sub>% of carbon, after which the carbon curve increases to a maximum of 0·36% in the core at  $5\frac{1}{4}$  in. from the outer edge. The bulk of the core zone averages 0·31–0·32% of carbon, decreasing towards the centre to 0·28% of carbon. As might be expected, the oxygen contents are decidedly lower than in a rimming steel of lower carbon content. Although the oxygen results at selected points across the ingot slice are generally of a low order, the trend of the variations resembles that of a normal rimming steel, being high at the outer edge, decreasing to a minimum and finally maintaining a steady value in the core. The highest oxygen value is that of sample No. 3 in the indeterminate zone, where blow-holes and general unsoundness are at a maximum.

*Summary and Observations.*

This ingot of 0·29% carbon steel has several features which differ from those of a normal low-carbon rimming-steel ingot, such as the unusual appearance of the rimming action, the presence of columnar crystals and the variation in carbon content. It does, however, provide a definite answer to the question as to whether the iron in the rim portion has been deposited as  $\delta$ -iron. It is shown that the rim contains essentially about 0·25% of carbon, and it is submitted that this could not have been deposited in the form of primary crystals of  $\delta$ -iron.

No satisfactory explanation can be submitted for the occurrence of lower carbon contents (below 0·2%) in the outer skin of this ingot to a depth of about  $\frac{1}{4}$  in.<sup>1</sup>

<sup>1</sup> Mr. Mitchell has subsequently communicated a further note on this point. Three further casts were selected containing respectively 0·28%, 0·32% and 0·31% of carbon, and one ingot of each was drilled at eleven positions,  $\frac{1}{4}$  in. deep, with a  $\frac{1}{2}$ -in. drill, at the mid-point of the ingot length. In each case the carbon contents were confirmatory of those obtained in the outer skin of the ingot reported upon in the paper.

[This paper was discussed jointly with the preceding one by D. Binnie on "A Study of a Shell-Steel Ingot."]

## JOINT DISCUSSION.

The papers by D. Binnie on "A Study of a Shell-Steel Ingot" and by T. Swinden on "The Examination of a Rimming-Steel Ingot containing 0·29% of Carbon" were discussed jointly.

**Dr. L. NORTHCOTT** (Teddington) : In introducing his paper Dr. Binnie said that he had a number of theories as to the formation of the zoned structure at the bottom of the ingot. The value of the paper would have been greatly enhanced if those theories had been given for discussion on the present occasion. Two suggestions may be put forward as to the cause of zoning. I take it that Dr. Binnie is fully satisfied by the appearance of the structures and the high carbon content of the steel that it is not evidence of a rimming action. The double rim would correspond to what is sometimes observed as a double rim in a rimming steel.

The alternative suggestion is that the zoning at the bottom is an artificial periodic effect arising from a change in turbulence at the bottom of the ingot. It is difficult to know exactly what happens when a liquid stream enters a mould. Presumably the metal rises up the sides, as at *a* of Fig. A, in the early stages of pouring. Later, when there is a fair quantity of liquid in the mould, it has been shown that the general action is for the liquid to rise in the centre, then divide and come round as shown at *b*. In other words, at some stage there is a change in the direction of movement of the liquid metal near the mould wall, and it is known that a change in turbulence can give rise to segregation effects.

I think that the ferrite spots in the ingot are merely an indication of the dendritic structure of the ingot. It is fairly well known that in a metal crystal where there are innumerable sub-branches of the dendritic structure, there will be disconnected spots of the last material to freeze. It is fairly well established, I think, that that is shown in the cast structure and it frequently persists beyond the cast structure, the areas consisting of material rich in phosphorus and sulphur inclusions. It is also known that the phosphorus-rich portions are usually low in carbon. Therefore, in view of the raising of the critical point due to the presence of phosphorus, ferrite is precipitated on the phosphorus-rich portions, and the interconnection which Dr. Binnie makes with the inclusions is not that the ferrite precipitates on the inclusions but that they both occur at the same spot. In Figs. 12 and 32 and on the right-hand side of Fig. 42 there is something equivalent to a dendritic structure shown by the ferrite spots.

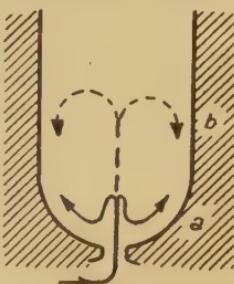


FIG. A.—Flow of Molten Metal entering Mould.

Turning to Dr. Swinden's paper, in the  $\delta$  region of the iron-carbon alloys the limit of solid solubility of carbon in iron to give  $\delta$  is about 0·1%. The peritectic occurs at about 0·2%; the effect of manganese, of which there is 0·4% in Dr. Swinden's ingot, is not accurately known, but the indication is that the peritectic point would be moved somewhat to the right. The limit of the  $\delta +$  liquid region is at about 0·5% carbon. I would ask Dr. Swinden: If this material does not solidify as  $\delta$ -iron in the first instance, as what does it solidify? I certainly hold no brief for the  $\delta$ -iron theory as the cause of the formation of rimming steel, but it would be useful for someone to prepare a rimming steel with more than about 0·5% of carbon, so that there would be no question of  $\delta$ -iron solidifying from the melt, since the first crystals to separate could be of  $\gamma$ -iron.

Mr. J. H. WHITELEY (Consett Iron Co., Ltd., Consett, Co. Durham): The ingot which Dr. Binnie has described exhibits in its microstructure three features of particular interest. The first is the white bands that appear in the sulphur print at and near the skin; the second is the complex granular structure, and the third the white spots which occur in the columnar zone. My remarks will be confined to the last two effects, as on the first-mentioned I have nothing at present to say. The excellent photographs of the etched sections seem to indicate that three different sets of crystals had formed in the ingot as it solidified and cooled. The primary crystals which developed during freezing are clearly shown in the cupric-etch illustrations. Then there is a set of grains which are outlined by narrow ferrite borders. Frequently these grains contain two or more dendrites and sometimes a ferrite border cuts right across a dendrite, so that the two sets of crystals are obviously not identical. Yet, it is clear that the primary crystals had some influence on the growth of the secondary grains, for the latter are elongated in the columnar zone and equi-axed in the central part of the ingot. The grains of what seems to be a third set are of smaller size. They have no ferrite borders and produce an effect which somewhat resembles spangling. I at first thought that this feature was simply due to different orientations of the pearlite laminæ in the grains of the second set, the pearlite having developed from more than one point at the boundary of each grain, but, on a close examination of the illustrations, I observed several instances where one of the spangling grains apparently crosses a ferrite line. It looks, therefore, as though a third set of grains is really present, and it is an intriguing question as to which set has the greatest influence on the physical properties of the steel.

Dealing now with the white spots, a careful comparison of the structures as revealed by nitric acid and by cupric etching shows that the spots generally occur well within the segregated areas of

the cored structure. Now, where phosphorus and probably other elements which may be in solid solution are concentrated, the temperature at which ferrite begins to appear in cooling is raised, and, whilst it separates most easily at the grain boundaries, it may also form at phosphorus-rich areas within the grains, provided that the carbon content is not too high. Hence, I consider that the white spots represent those portions of the steel which were last to freeze. At such places the segregation would be the most intense, and in this connection it should be noted that the white spots almost invariably contain one or more MnS inclusions. The absence of white spots from the central equi-axed zone, notwithstanding its slower rate of cooling through the critical range, can be explained by the slower rate of solidification which would there obtain. At and just below the solidus of medium-carbon steels phosphorus diffuses more rapidly than at lower temperatures, and its concentration in the final portions to freeze would thus be diminished.

Referring to Dr. Swinden's paper, Mr. Whiteley said : I am particularly interested in this example of a rimming-steel ingot, because, although I have been engaged all my life in the manufacture of mild steel for plates and sections, I have never witnessed the making of a cast of such steel which rimmed during solidification. Yet time and again I have seen casts tapped in an apparently over-oxidised condition. Unfortunately, the oxygen in the pit sample is not given, but I calculated from the average loss of carbon in the rim, as judged from the pit-sample result and the relative volumes of rim and core, that between 0·004 and 0·005% of carbon was liberated as carbon monoxide during freezing, so that the oxygen content of the steel when tapped would not be more than 0·013%. That figure surprised me, for I expected at least 0·02%. Now, in another paper on rimming steel presented to this Meeting by Swinden, Stevenson and Speight,<sup>1</sup> the authors have given the percentages of oxygen in the pit samples of five rimming casts with carbon contents ranging from 0·04 to 0·14%. Further, some years ago the Committee on the Heterogeneity of Steel Ingots described a rimming steel ingot (No. 62)<sup>2</sup> with only 0·03% of carbon, and the oxygen content of that ingot was later ascertained by Andrew and his co-workers to be about 0·110%.<sup>3</sup> Thus, several examples were available, the oxygen and carbon contents of which when in the ladle were known with fair accuracy, and on plotting the one against the other I obtained the curve shown in Fig. B. It has a marked resemblance to a rectangular hyperbola and, if

<sup>1</sup> "Rimming Steel.—An Examination of the Carbon and Oxygen Relationship in the Solidification of Basic Open-Hearth Steel," *Journal of The Iron and Steel Institute*, 1944, No. I., p. 331 P.

<sup>2</sup> Fifth Report of the Committee on the Heterogeneity of Steel Ingots, p. 32, *The Iron and Steel Institute*, 1933, *Special Report No. 4*.

<sup>3</sup> J. H. Andrew, T. Raine and J. B. Vickers, Sixth Report on the Heterogeneity of Steel Ingots, Section III., p. 67, *The Iron and Steel Institute*, 1935, *Special Report No. 9*.

actually one, it would mean that in steels which rim well the product of  $(O) \times (C)$  is a constant. The first and last points on the curve are, however, not in good agreement with that inference, for the  $(O) \times (C)$  values for those steels are more than 50% higher than for the other five. As to the 0.03% carbon steel, there can be little doubt that its oxygen content was excessive, since a considerable amount of aluminium was added to the ladle.

To obtain the constant shown by the five intermediate steels the oxygen should be about 0.075%, and it seems reasonable to assume that if that amount

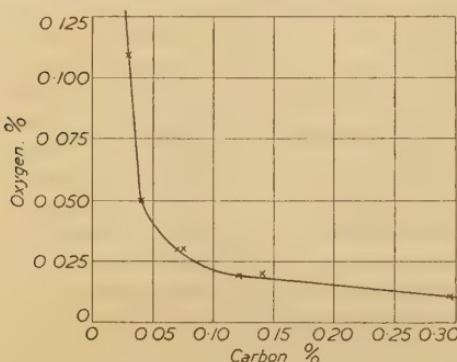
FIG. B.—CARBON-OXYGEN RELATIONSHIP.

had been present the steel would have rimmed properly without any addition of aluminium. On the other hand, the 0.29% carbon ingot is an exception which cannot be explained in that manner, since to give the required constant its oxygen content should not be above 0.008%. Nevertheless, it seems clear that to obtain a steel which rims well the oxygen content must increase as the carbon is reduced and that the relationship is not linear.

That the presence of oxygen in the steel is essential for the production of a rimming quality is, I think, beyond question, and a comparison of the sulphur prints and macro-prints of these seven ingots suggests that the difference between the rim and core becomes more pronounced as the oxygen content of the steel rises, for this change, if real, does not seem to be connected with the carbon, sulphur and phosphorus contents. Hence, it may be that the etching difference between rim and core is mainly due to the presence of more oxygen in solid solution in the rim. If that is the case the amount must be very small even in the rim, since the Oxygen Sub-Committee have shown that in this type of steel 90% or more of the oxygen is contained in the inclusions.<sup>1</sup> The idea that very small quantities of oxygen may have a marked effect on the etching reactions should not be lightly dismissed, however, especially as it is now an established fact that an addition of less than 0.003% of boron sometimes increases considerably the hardening property of steel.

Dr. C. H. DESCH, F.R.S. (Vice-President; London), discussing Dr. Binnie's paper, said : It is a curious fact that according to the

<sup>1</sup> Andrew, Raine and Vickers, *loc. cit.* T. Swinden, W. W. Stevenson and G. E. Speight, Third Report of the Oxygen Sub-Committee, Section II., Part B, *Journal of The Iron and Steel Institute*, 1941, No. I., p. 312 p.



analyses made by Dr. Swinden and his staff the light and dark zones show scarcely any difference in either carbon or sulphur content and yet there is this great difference in the sulphur print. The sulphur print, of course, does not give a quantitative representation of the amount of sulphur that is present. The size of the particles affects very much the intensity of the spots that are produced, and it would be very interesting to make a more detailed study under the microscope of these zones. At the National Physical Laboratory a few years ago, when we were trying to determine whether there was any appreciable solid solubility of sulphide in ferrite, we found that very often when the particles were small it was extremely difficult to see under the microscope just how many particles of sulphide were present, but that, if the surfaces were carefully prepared and a sulphur print was taken and examined under the microscope, we obtained very much more information. I think it may be found that the difference between the light and dark zones in the sulphur print is due not to any difference in the amount of sulphur but to its distribution. I know that Mr. Whiteley has found some qualitative evidence of solid solubility, and Professor Portevin has produced some qualitative evidence in its favour, but we could never determine it, partly because in ingots made from pure iron and pure sulphur of a definite composition the segregation is so great that one does not find an area in which the true percentage of sulphur can be ascertained with certainty.

With regard to zones, Dr. Northcott's suggestion of a change in the character of the turbulence was an interesting one, but it would apply only, of course, to a bottom-run ingot, and I remember that, when the first paper that we ever had on macro-etching was given to us by Mr. Humfrey at the end of the last war, some of his prints, taken by his printing-ink method, showed similar zones from a top-cast ingot.

Dr. NORTHCOTT : I think Mr. Humfrey's banding effect was what I should call a periodic effect and different from Dr. Binnie's experience.

Dr. DESCH : I was speaking from memory. With reference to a remark that Dr. Northcott made on Dr. Swinden's paper, I came across the other day, in some notes that I had made during a discussion on rimming steel at a committee meeting, a statement made by one speaker that he had prepared a rimming steel with 0·6% of carbon. I have not been able to verify that by reference to the Minutes of the meeting in question, but, if correct, it has a considerable bearing on this point. I have never seen anything like a 0·6% carbon rimming steel, but we once produced a rimming steel with 0·3% of carbon in the course of a  $1\frac{1}{2}$ -ton cast.

Mr. R. A. HACKING (Messrs. Dorman, Long & Co., Ltd.,

Middlesbrough) : Looking back through the literature, one finds a number of examples of the zoning effect prominently displayed in Dr. Binnie's sulphur prints. There are several examples in Hultgren and Phragmén's paper on rimming steel,<sup>1</sup> in which work they seem equally visible on macro-etched sections. In most of the ingots examined by these Swedish investigators the zones were considerably narrower but much more numerous than in Dr. Binnie's ingot—a feature which would be expected from the fact that they were small ingots top-teemed at fairly high speeds. In Dr. Northcott's paper on the "Influence of Turbulence upon the Structural Properties of Steel Ingots"<sup>2</sup> there is the case of an ingot which was stirred during solidification, and in which a pronounced zoning effect was obtained, although possibly it was not quite the same as in Dr. Binnie's ingot. I agree with the opinion which Dr. Northcott has expressed in to-day's discussion that turbulence during the filling of the mould is the principal cause of the zoning effect. As currents impressed mechanically upon the system by the teeming stream die away, convection currents possibly come into the picture, but the former would be expected to have much the greater influence. Why the zones should show up much more clearly in the second than in the first sulphur print and be almost invisible in the macro-etches I am not prepared to say, but it does stress the fact which Dr. Desch has mentioned, and which we have all tried to bear in mind since the early days of the Committee on the Heterogeneity of Steel Ingots, that sulphur prints do not give quantitative results. On reflection, one could hardly expect them to do so, since the technique of sulphur-printing involves a limited time factor, a limited amount of one reactant, and a steel surface which is progressively stifled with reaction products. Dr. Swinden's quantitative inclusion counts for oxides and sulphides are noteworthy, and the greater occurrence of sulphides in conjunction with the known solubility of manganese sulphide in dilute acids<sup>3</sup> has, in my opinion, a significant bearing upon the zoning effect and the greater contrast provided by the second prints.

In connection with Dr. Desch's remarks on Dr. Swinden's paper, the sulphur prints to which he refers were exhibited by me to the Ingots Committee some years ago. I had noticed that last ingots from 100-ton casts of high-carbon steel showed, on occasion, a peculiar effect during solidification, whereas the remaining ingots from the same cast were quiescent and drew strongly in the heads as intended. Sections corresponding to the top, middle and bottom of a typical effervescent last ingot were cut from 8-in. square blooms rolled from the same. Without previously divulging the carbon content of the steel, sulphur prints from these sections were

<sup>1</sup> American Institute of Mining and Metallurgical Engineers, 1939, Contribution No. 112, pp. 57, 65, 78.

<sup>2</sup> Journal of The Iron and Steel Institute, 1941, No. I., p. 49 p.

<sup>3</sup> E. F. Law, Journal of The Iron and Steel Institute, 1907, No. II., p. 94.

passed around the table, and the opinion was unanimous that they showed all the characteristics of a rimming steel—whereupon the carbon content was revealed as 0·7% ! I will certainly try to obtain some further evidence of this phenomenon, preferably from an ingot as cast, together with other relevant data, such as the analysis of the nozzle slag, &c. Some little time may elapse, and several abortive attempts be incurred, before a really good example comes to light, but the work will be well worth while if it helps to solve the vexed question of the part played by the  $\delta$ -phase in rimming steels.

Dr. E. W. FELL (Northern Aluminium Co., Ltd., Birmingham) : I should like to discuss the presence of the prominent white and dark bands seen sometimes in sulphur prints of steel and illustrated in Fig. 36 of Dr. Binnie's paper. Similar bands are found after steel has been rolled into billets, so the phenomenon is persistent and the structure associated with it is a stable one. The different behaviour of the metal in the white and dark bands is also shown by sections of the rolled bar etched, I believe, for some time in hot acid solution, which results in the dark bands being more attacked by the acid while the white ones are left sharply in relief. The phenomenon is also known in the trade as "rim" or "ring" segregate. It is not confined to the plain carbon steels but occurs, for example, in 5% nickel steel. I believe it has been found impossible to get rid of it by modifications of ingot casting procedure. I have never heard of the usual mechanical properties of the steel being adversely affected by the presence of the bands, but the sight of them is alarming.

Chemical analyses of my own on drilled samples showed no marked difference in total sulphur content between the various bands, thus supporting the findings in Table IV. The observation, in Dr. Swinden's contribution to the paper, that a count of sulphide inclusions over the dark zones yields larger sums than when taken over the white zones, is interesting. The presence of sulphides in varying forms seems to be in accordance with the stability of the bands during rolling, and it may therefore be anticipated that heat treatment will produce no change. In passing, I may say that the value of 6·0 for sulphides in the second row of figures in Table VI. may be somewhat low, since the zone described as No. 2 shows clearly in Fig. 63 a thin white zone situated along its centre, which may have affected that particular count.

As to the cause of banding, the phenomenon seems to be associated with great chilling during solidification. The rate of solidification will be greatest at the bottom of the ingot, as there the mould is cold and thicker, and the metal entering it at the start is colder owing to heat lost on passing along the narrow runner passage. It will be seen in Fig. 3 that the white bands approach the sides of the ingot on passing up the ingot, disappearing about

half-way up, and the chilling will decrease on passing upwards owing to the steadily increasing temperature of the mould wall caused by the presence of a mass of molten steel. Thus an apparent measure of the amount of severe chilling at any point on the side of the ingot is the depth of the innermost white band there, below which the rest of the ingot may be regarded as an ideal ingot, that is, one which has cooled just slowly enough to avoid banding.

Let the rate of solidification, as measured by the motion inwards of the boundary between the solid and liquid steel in a direction normal to the surface of the mould be given by  $ds/dt$ , where  $s$  is the distance from the side of the ingot and  $t$  is the time. If this rate is given by the periodic curve shown in Fig. C, for example,

then the points where the line  $ab$  cuts the curve represent the joins of the white and dark zones in the sulphur print of section  $5b_2$  in Fig. 58; only if the curve lies above the line does the steel correspond to that in a white zone, i.e., where the rate is greater. Similarly, the points where the line  $cd$  cuts the curve represent the boundaries of the zones of scattered ferrite crystals, and the rate is considered to be sufficiently slow to ensure conditions for

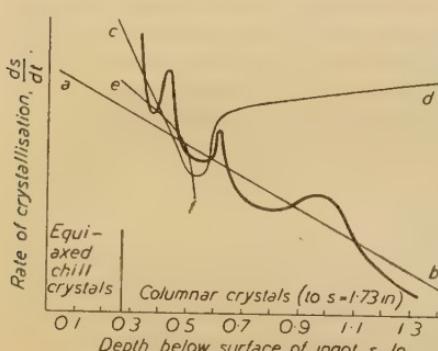


FIG. C.—Periodic Structures in Ingots.

the crystals to form only if the curve lies below the line. The points where the line  $ef$  cuts the curve refer to the distribution of sulphides and silicates, as shown in Figs. 52 to 56, which are regarded as more in evidence only when the curve lies below the line.

The fact that sulphide inclusions were more in evidence in the dark bands than in the white bands suggests that slower solidification gave time for the sulphide inclusions to form and to coalesce with one another, but the sulphide in the white bands seems to be in a more unseparated state owing to relatively quick solidification. The thin zone of ferrite crystals at 0.37 in. below the ingot surface of section No. 5 and their reappearance at 0.58 in. suggest that their formation was helped by slower solidification, and similarly for the larger sulphide and silicate inclusions at 0.35 in. and 0.46 in. below the surface. The ferrite crystals seen in Fig. 47 have a fresh appearance and those in Fig. 49 perhaps less so, but in Fig. 50 at 1.18 in. depth their surface appears to be more rounded, which suggests that they have begun to diffuse and disappear entirely if the cooling is slower still.

The periodic curve of Fig. C consists of fluctuations in solidification superimposed on a normal smooth cooling curve involving only change of temperature. The lines  $ab$ ,  $cd$  and  $ef$  differ from

each other, which is not surprising, as the points where they cut the curve are on the edges of fields in which different reactions occur. The zones indicate that these physico-chemical reactions are highly sensitive.

I would suggest, tentatively, that the periodicity in properties is the result of metastable conditions during solidification, such as may arise on undercooling of the liquid by severe chilling. The ring structure seen in Fig. 38 is probably connected with unsteady solidification. Many examples are known of periodic crystallisation in pure inorganic and organic substances. The layer, which may be denoted by  $l_1$ , of equi-axed chill crystals is supposed to be very quickly formed from a spatial distribution of nuclei, as the liquid steel was in a labile state owing to very rapid cooling. The columnar crystals grow, since the adjacent liquid layer  $l_2$  is metastable—not labile, because freezing occurs to a higher temperature than in layer  $l_1$ —and so their rate of growth is less. Meanwhile, the liquid in an adjacent layer  $l_3$  is becoming more metastable, owing to cooling by heat conduction through the partly liquid layer  $l_2$  and also by heat passing upwards continually from the liquid into the air. The result is that the columnar crystals begin to grow faster in layer  $l_3$ , but after a time this rate will decrease as they penetrate a hotter adjacent layer  $l_4$  which is less metastable. This process is repeated and has probably considerably diminished by the time the columnar crystals finally stop growing. Alternations in the rate of growth would be associated with periodic evolutions of heat of crystallisation, and so heat waves will approach the ingot/mould interface. Such waves might be detected; the higher the sensitivity and speed of recording of the apparatus used for the purpose, the better would be the opportunity of determining them. The end of a thermocouple might be placed at a distance of  $\frac{3}{8}$  in. from the mould face and inside the ingot space, choosing a cast where banding is usually present.

This supports the view that growth into the liquid steel of the dendrites of the columnar zone was pulsatory. However, since a high freezing rate is assumed to be necessary for banding to occur, I would recommend that an experiment be made to discover the effect of altering the "chill" near the bottom of the mould. I suggest that a square cavity, say, 5 in. by 5 in., be machined from the outside of a mould and to such a depth that the remaining wall is only just thick enough to hold during the casting of an ingot; a suitable place would be at and above but not below the position of section No. 4, and on a mould face. Further, heat-insulating material might be placed in the cavity. The chill on the molten steel should thereby be much reduced near the cavity. Sulphur prints of nearby ingot sections would be interesting and may show the disposition of the bands, and acid etches the disposition of the ferrite spots, in relation to the area of reduced chilling.

I would ask the author how the two zones of ferrite crystals in

section No. 4 vary in position on passing up to No. 3, where only one zone extending, say, to a depth of 1·06 in. is present. Is not the presence of scattered ferrite crystals in the columnar zone of section No. 2 continuous with their presence in No. 3, rather than being fortuitous, as stated?

Dr. Desch has just referred to some macroprints of Humfrey's. May I confirm that the zoning shown in Fig. 38 near the surface of the ingot is similar to the ring structure in those top-poured ingots? <sup>1</sup>

(Contributed later in writing). It would be a valuable addition to the paper if Dr. Binnie included in his reply a sulphur print of an axial section of the steel within, and in the neighbourhood of, the small taper fireclay sleeve, because on inspection of the extreme left-hand side of Fig. 3, in the lower half of the section shown, there appear to be two thin white zones situated close together and inclined at an angle of about  $13^{\circ}$  to the ingot axis. The contours of these and of other zones nearby have a flow-lined appearance with respect to the sleeve. A sulphur print on a larger scale than Fig. 3 would reveal clearly the zoning referred to.

#### JOINT CORRESPONDENCE.

Dr. D. BINNIE (The Lancashire Steel Corporation, Ltd., Irlam near Manchester) wrote: The paper by Dr. Swinden shows that in a rimming steel of 0·29% carbon content the rimming action, while still active as measured by the intensity of the rim-core junction, is losing its power.

There is no reason for assuming that a primary precipitation of  $\delta$ -iron is necessary for rimming to occur. Dr. Swinden's paper clarifies this point, but it must not be lost sight of that the precipitation of  $\delta$ -iron might still have an influence on the composition of the resulting rim. For example, the carbon analysis in the rim of a steel which freezes initially largely as  $\delta$ -iron might be lower than if the  $\delta$ -iron transformation had not existed. Such a point would not be easy to prove, but the view expressed by members of the Ingot Committee that the lower carbon analysis of the skin of the 0·29% carbon ingot might be due to primary precipitation of this purer  $\delta$ -iron is theoretically possible and should be capable of verification when higher-carbon rimming steels are examined.

I notice that the carbon analyses, especially of the metal just inside the core, are higher than the pit-sample figure. This follows from the Hultgren and Phragmén hypothesis.

Could the author, by analyses at a few points at least in the

<sup>1</sup> Compare with *Journal of The Iron and Steel Institute*, 1919, No. I., p. 273, Print 3 and Fig. 3.

core of the lower portion of the ingot, confirm that the pile-up of carbon in the core occurs in that portion also?

Mr. S. W. EVANS (Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd., Cardiff) wrote: It would have been most interesting to have had the oxygen content of the pit sample of Dr. Swinden's ingot. The sluggish rimming, described by Dr. Swinden as a "boil," is similar in appearance to the action of low-carbon rimming steel which is in an over-oxidised condition and requires the addition of aluminium.

High-carbon rimming steel might not evolve sufficient gas to keep the surface liquid (as a result of the metal current) if its composition falls below the line *NZO* of Hultgren and Phragmén's carbon-oxygen equilibrium diagram; that is to say, for sufficient gas to be evolved, the steel must contain more carbon and oxygen than would be present under equilibrium conditions. It can definitely be stated that basic open-hearth high-carbon rimming steels are best made by first reducing the carbon to under 0.1% and then "coaling up" in the ladle. If the carbon is "caught" at the desired figure, then the rimming action is very poor and the steel is thin-skinned, the primary blow-holes being very close to the surface.

From the carbon graph in Fig. 1, the impression of a double rim is apparent. Full details of the rimming action would perhaps shed some light on this. The carbon has risen to a peak of 0.306% in the indeterminate zone and then fallen to 0.263%, to rise again in the core proper. It is interesting to note that the carbon-oxygen product at the first peak,  $2\frac{7}{16}$  in. from the outside, amounts to 0.004, which is 1.6 times 0.0025, 1.6 atm. being approximately the pressure that one would expect at the middle of a 6-ft. ingot. This suggests that the ingot top had frozen over, the increased pressure then preventing the evolution of gas, and later breaking the crust to allow rimming to recommence.

### AUTHORS' REPLIES.

(Figs. D to H = Plates XXXIII A and XXXIII B.)

Dr. BINNIE wrote in reply: Referring to Dr. Northcott's contribution, rimming actions can be present in ingots of higher carbon content than the one described in the paper, but the rimming action is readily detected by chemical analysis; again, a limited rimming action in high-carbon ingots is more prevalent at the top than at the bottom. Hence, I do not think that a rimming action has been responsible for the zoning.

Dr. Northcott and Mr. Hacking consider that turbulence might be a prominent factor in causing the zoning, but I am not at all convinced of this. Zoning is present in top-cast as well as in bottom-

cast ingots, the only difference being that in the latter the zoning can be more symmetrical in following the contours of the ingot mould. The surface agitation associated with top-casting, I consider, partly breaks down the symmetrical nature of the zoning. I am sure that if turbulence has been a prime factor in zone formation the zones would not have followed so closely the contour of the mould, especially at the mould corners, *see* Fig. 28.

Dr. Northcott and Dr. Whiteley look on the white spots as an indication of the cored dendritic structure of the ingot and agree that they might be due to local spots rich in phosphorus or some other constituent. The white spots are absent from the chill equiaxed crystals; they can be absent in the earlier stages of columnar crystals and directional primary crystals; only odd ones can be seen at the centre of the ingot, and they are sensibly absent from the feeder head. A simple normalising treatment is sufficient to remove them, and such experiments as have been tried to bring them back by slow cooling from normalising temperatures have so far not met with success. Soaking at 1200° C., an experiment suggested by Dr. Whiteley, brought back some white spots in a specimen previously normalised to remove them.

Dr. Fell draws attention to the rounded nature of the white spots in Fig. 50. The ferritic grain boundary to the right of Fig. 50 looks like a string of white spots joined together. A review of Figs. 46 to 57 shows a connection or at least an association of the white spots with non-metallic inclusion forms, and beyond this not much more can be said just now. The ease with which they are removed by normalising suggests that they are no different in composition or constitution from the ferritic grain boundaries.

Dr. Desch and Mr. Hacking point out the limitations to be expected from the established sulphur-printing technique. The zones show up well on a "first" sulphur print, provided that the surface to be printed has been given a high polish (a 4-min. contact is desirable to bring out the zoning on a first print), and the "second" print on this surface shows the zoning even more markedly. With an ordinary production surface finish the zones are not at all clear on first sulphur print, but require a second print to expose them. Many sulphur print tests, made with widely different strengths of acids, have not yielded useful information on the development of the zones.

The "rim" or "ring" segregate described by Dr. Fell is similar to the zoning shown in sulphur-printing. A sample of the ingot corresponding to that shown in Fig. 38 was heated for 45 min. in a mixture of 50% concentrated hydrochloric acid and 50% water by volume at 78° C. The zones, as shown by a previous sulphur print, were clearly revealed (*see* Fig. D, macro-etch); a zone corresponding to the depth of the columnar crystals is also seen. Fig. E is the sulphur print of a section of a 5½-in. billet from another cast of the same type of steel, bottom-teemed, cut from close to

## SHELL STEEL INGOTS.

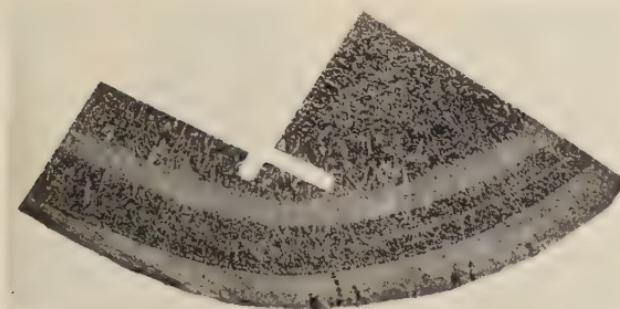


FIG. D.—Macro-Etch of Section corresponding to Fig. 38; heated 45 min.  
in 50% hydrochloric acid at 78° C.

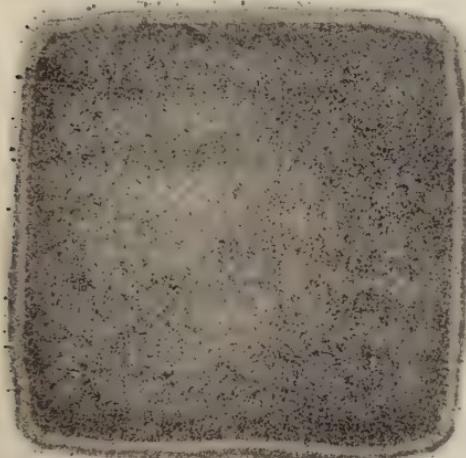


FIG. E.—Sulphur Print of a Section of a 5½-in. Billet from  
the bottom of a bottom-teemed ingot.



FIG. F.—Macro-Etch (45 min. at 78° C. in 50% hydrochloric acid) of  
Billet Section shown in Fig. E.

[*Binnie, Author's Reply.*  
[To face p. 390 p]

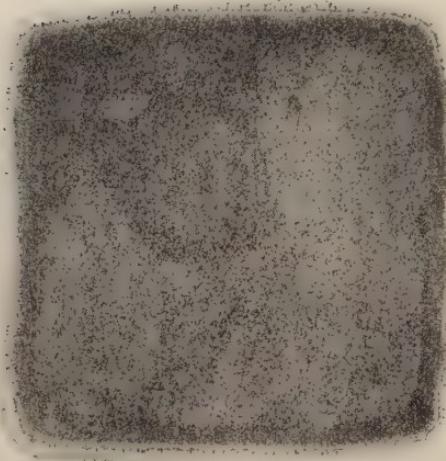


FIG. G.—Sulphur Print of a Section of a  $5\frac{1}{2}$ -in. Billet from the bottom of a top-cast ingot.



FIG. H.—Enlargement of Sulphur Print of the Ingot Section (see Fig. 3), showing zoning at bottom runner feed position.

[*Binnie, Author's Reply.*  
[To face p. 391 p]

the bottom end of the ingot. The zoning is clearly shown to be similar to the zoning of the ingot described in the paper. This billet section was heated in acid as above, when the ring segregate was exposed, *see* Fig. F; a thin white line similar to the one dividing zone 2, dark, in Fig. 58 is also seen. Fig. G is a sulphur print of a 5½-in. billet from the bottom of a top-cast ingot.

Other methods of macro-etching do not bring out the zones, but apparently show zones of a different form, as in Fig. 38. The zoning of the ingot surface developed by swabbing with dilute nitric acid was similar to that shown in Fig. 3.

Dr. Desch, Mr. Hacking and Dr. Fell draw attention to examples of zoning throughout the literature. The zoning seen on sulphur-printing appears to correspond to that revealed by macro-etching, but only when the macro-etching has been drastic. Humfrey, in the paper referred to by Dr. Desch and Dr. Fell, states that the general effect of strong-acid etching closely follows that obtained by sulphur-printing.

The zoning shown in the papers referred to occurred in small ingots and a strict comparison does not hold; nevertheless, the zoning on those ingots will, no doubt, be related to that on the present ingot.

I am in agreement with Dr. Fell that the zoning is attributable to chill. His Fig. C represents what might have occurred, and his ensuing arguments on zone formation are well worth studying. In reply to Dr. Fell, I do not know at the moment how the two zones of ferrite crystals in section No. 4 vary on passing up to No. 3, but sections are being prepared to establish this point.

Fig. H was taken from the sulphur print of the ingot (*see* Fig. 3) and shows in more detail the zoning at the bottom runner feed position. Apparently the run of hot metal during teeming did not remove the zoning locally.

The mechanical properties of the steel are not adversely affected by the zones, except the outer white zone, which is unsound metal :

			Max. Stress, Tons per sq. in.	Elongation, %.
Zone 1, light	:	.	39	10
2, dark	:	:	46	20
3, light	:	:	47	25
Beyond zone 3, dark	:	:	46	15

The tensometer tests were made on the normalised sample.

Dr. SWINDEW wrote in reply : It is gratifying to read the interesting and thoughtful contributions which unfortunately through illness I was unable to hear personally.

Dr. Binnie will no doubt reply in detail to the discussion of his paper, with particular reference to the explanation of the zoning. Dr. Northcott, Mr. Hacking and Dr. Fell suggest hypotheses based on turbulence and/or differences in the chilling effect of the mould.

The detailed statement by the last-named, advancing the view that the growth of the dendrites in the columnar zone is pulsatory in character is very interesting.

The evidence appears strongly to support the basic idea that the zoning is due to variations in the rate of solidification of the respective zones, and is explained, as regards the sulphides, if one assumes the presence in the white zones of sub-microscopical particles which have not had sufficient time to coalesce.

It is important to recognise this further demonstration that the sulphur print, as normally taken, does not necessarily give a true picture of the sulphides present, but is dependent on particle size. Those who have worked on weld metal will readily subscribe to this view.

However, regarding the primary cause of this differential cooling, the evidence is less conclusive. It is possible that temporary obstructions of varying duration in the steady teeming rate are responsible for the zoning. The observation of Dr. Desch regarding the occurrence in top-cast ingots can definitely be supported. Undoubtedly, turbulence plays an important part, and the graphical reconstruction of the problem by Dr. Fell, who further combines with the differential-chilling idea considerations of the metastable liquid condition, is most instructive. The suggested experiment in a mould of varying degrees of chill should throw more light on this interesting phenomenon.

Turning to the note on the 0·29% carbon rimming-steel ingot, the fact that the precipitation of  $\delta$ -iron might have an effect on the composition of the rim is not in question. The only point established is that, as the rim in this case contains about 0·25% of carbon, it could not have solidified initially as  $\delta$ -iron. This does not preclude the possibility of  $\delta$ -iron being deposited and being transformed subsequently by reaction with the interstitial mother-liquor to the composition subsequently found. May I repeat that the investigation was made because it had been asserted that the basic and primary reason for the characteristic rim and core structure of rimming steel was that the iron in the rim portion was deposited as  $\delta$ -iron. The evidence put forward in support was that the carbon content of the rim *never* exceeded the postulated carbon content of  $\delta$ -iron. For the reasons stated in the paper, I do not subscribe to this view, and the facts now established appear definitely to contradict it.

I well remember seeing the data on the 0·76% carbon ingot presented by Mr. Hacking to which Dr. Desch and he refer, and earnestly hope that this can be followed up as suggested.

Mr. Whiteley's remarks are, as usual, indicative of a careful study of the data presented in these two papers. With regard to his discussion of the carbon and oxygen relationship in rimming steel, I am in agreement with Mr. Whiteley's considerations; in fact, I have discussed the interdependence of these two elements in the

rimming action on several occasions. One does not, however, quite see the evidence for Mr. Whiteley's conception of the difference in the etching properties of rim and core as due to the presence of *more* dissolved oxygen in the rim. Work at the National Physical Laboratory shows that the dissolved oxygen in *pure* iron is very low, *i.e.*, between 0.003 and 0.006%, and the influence of carbon and manganese will undoubtedly be in the direction of reducing this quantity of dissolved oxygen.

Replying to Mr. Evans, it is regretted that the pit sample for this cast was not available. His observations on the practical aspects of making high-carbon rimming steel in the basic open-hearth are noted with particular interest.



# THE HEATING OF OPEN-HEARTH FURNACES WITH MIXED COKE-OVEN AND BLAST-FURNACE GAS.\*

BY R. W. EVANS, B.MET. (MESSRS. GUEST KEEN BALDWINS IRON AND STEEL CO., LTD., PORT TALBOT, SOUTH WALES).

## SUMMARY.

The principles of flame development are discussed ; it is shown that high-temperature flames are the result of rapid combustion. The rôle of the flame in an open-hearth furnace during (1) melting and (2) refining the charge is described, with a note on refining with non-luminous flames ; refining with a non-luminous flame renders the process inflexible.

Slag foams are next discussed ; the foam is due to high surface tension in the slag, which can easily be reduced by the introduction of a more luminous flame—hence foams are due more to the nature of the flame than to that of the slag. Foaming slags react seriously on output and furnace wear.

The development of luminosity in mixed coke-oven and blast-furnace gas flames is due to the cracking of hydrocarbons, and the degree of luminosity that may be expected from a given mixture is shown. The nature of the cracking and of the resulting carbon particles depends on the temperature ; the size of particles precipitated affects the degree of luminosity. Loss of calorific value in coke-oven gas owing to preheating is discussed, and it is suggested that it may be more efficient to preheat blast-furnace gas only, injecting the coke-oven gas cold with tar, &c., as an illuminant. The effect of moisture content is shown theoretically to have an adverse effect on luminosity.

Furnace design with particular reference to the gas port is discussed, with a note on port water-cooling, port slope and gas velocity. Different methods of introducing artificial illuminants are described. Mixed gases require plenty of air. Sloping back walls improve the roof life, but the roof should not be low.

The operation of mixed-gas furnaces is dealt with and the instrumentation is described. Dolomite consumption is less in mixed-gas than in producer-gas practice.

Metallurgically, mixed-gas furnaces do not oxidise the bath so readily, owing, it is suggested, to free hydrogen in contact with slag hindering the transference of oxygen to the slag. In conclusion, the author suggests that where the coke-oven gas is lean, it can more efficiently be injected cold with tar as an illuminant. Preheating of the air supply only is then necessary.

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IN an open-hearth furnace campaign, assuming that the source of heat is not lacking in either quality or quantity, a compromise is always being sought between two conflicting factors :

- (1) The rate of production.
- (2) The life of the furnace.

\* Received September 22, 1943.

Generally this means that the rate of production is kept up to the maximum commensurate with a reasonable repair cost and furnace life. If an effort is made to step up production by increasing the gas and air input, the probability is that the furnace life will be considerably reduced, with a very small increase in production, owing to the inability of the furnace to burn in the proper place all the gas delivered to it.

Decreased furnace life upsets regular production, and the schedule of furnace repairs is disturbed. This leads to furnaces being run for longer periods when they are already worn out, or to their having to undergo hasty patched repairs without thorough examination in a desperate effort to maintain production, all of which is only in the nature of postponing the evil day.

Therefore, to preserve an even production line, furnace lives must not fall below a certain minimum, and the furnaces cannot be driven at a higher rate than will allow this. Again, if the given furnace life is to be maintained, the average unit production must drop when high metallurgical loads are carried, or when considerable quantities of special or very soft steels are produced, or under any circumstances where long refining times are experienced. In any case, the management are generally trying to get the last ton out of the furnaces without affecting furnace lives, and as "the ice becomes very thin" at these critical rates, often it "gives way" and the result is a dent in the even line of production.

These considerations apply in a greater degree to furnaces using mixed gases than to those working on producer gas, as an operator who has worked both on the same furnaces will know. This is due to the greater incidence of slag foams in mixed-gas operation and the peculiarly accentuated attack of the flame and waste gases on silica brickwork.

It is to discuss the theory and practice of mixed-gas operation that this paper has been written. It takes into account twenty months' experience of mixed gases in a plant where during this period a change-over from 100% producer-gas to 100% mixed-gas working has been effected.

#### FLAME DEVELOPMENT.

It is both helpful and interesting to note the basic conceptions underlying flame development. The flame in an open-hearth or indeed any furnace is the path occupied by atoms of a combustible gas combining with atoms of oxygen, the chemical combination giving rise to an evolution of heat, which for unit volume of a given gas is constant. The resulting flame temperature, however, depends on various conditions, and primarily on the speed of combustion, *i.e.*, on the rate at which gas atoms collide and combine with oxygen atoms. It also depends on the rate at which the flame loses its heat to the surrounding atmosphere, which, in turn, is a function of the

specific heat of the waste gases and the emissivity of the flame. Where large numbers of gas and air atoms combine together quickly in a confined space, the great evolution of heat in the flame cannot be dissipated quickly enough; the result is an intense local build-up of heat, which is revealed as an increase in temperature.

Thus, in order to provide the most favourable conditions for high-temperature flames, the first aim is to give the gas and air atoms the greatest facilities for meeting each other. One way of promoting this is to deprive the gas of inert atoms, *e.g.*, nitrogen, which take part in intermolecular collisions without any resulting heat production. This may be done by substituting coke-oven gas for blast-furnace gas, *i.e.*, stepping up the calorific value; another way of reducing the proportion of inert atoms is to use oxygen instead of air, but this is not at present applicable to open-hearth furnaces.

The molecular motion in gases, where the intermolecular attraction is always very small, is definitely "translatory," as opposed to the motion in solids, which is "vibratory"; when a gas is heated the heat energy imparted to it is completely transformed into increased kinetic molecular energy, when the mean velocity of each molecule becomes increased by an increment which is nearly proportional to the increase in temperature above absolute zero ( $-273^{\circ}$  C.), at which temperature all molecular motion, translatory and vibratory, completely ceases.

As the molecular velocities increase, so the number of intermolecular collisions rises, and the number of impacts on the wall of a confining medium—*i.e.*, the pressure—is increased. If the gas is free it expands, owing to the outward rush of molecules. This gives the molecules greater searching power and increased probability of collision with oxygen particles; in an open-hearth furnace they have greater searching power and colliding probability owing to their own preheat. The net result is increased speed of combustion, which gives a higher flame temperature.

Finally, given the preheat in air and gas, the only means open to the designer of promoting the rate of molecular collision lies in so designing his ports that the maximum admixture of air and gas molecules is likely to result as soon as possible. This is the aim of the Venturi and the Maerz ports, in which respectively the gas is projected into an intensely directed air stream or the air is directed into the gas stream. The implication is also that the tongue between the gas and air ports should be as thin as is practically possible.

The velocity of gas entry also plays an important part in furnaces of conventional design. High-velocity gas on meeting the air stream produces increased "eddy" effects, leading to greater admixture. High flame temperature as a result of high gas velocity is achieved in the Hoesch furnace.

All attempts at increasing flame temperature, therefore, must be based on increasing the rate at which the gas and carbon atoms collide with oxygen atoms.

## THE RÔLE OF THE FLAME IN OPEN-HEARTH FURNACES.

Making steel in an open-hearth furnace can be divided into two consecutive stages :

- (1) Melting the charge—a physical process.
- (2) Refining the charge—a chemical process.

Practically only one type of flame is available, which has therefore to perform physical as well as chemical functions.

The physical process is relatively a simple one. It consists in imparting the maximum amount of heat from the flame to the charge and the minimum amount to the furnace structure. This is achieved by using the hottest flame attainable and keeping it as near to the charge as possible for the whole of its travel through the furnace. The transfer of heat is effected by both convection and radiation.

In the latter case the heat transferred in B.Th.U.'s per hour is proportional to :

$$(T_F)^4 - (T_S)^4$$

where  $T_F$  = absolute temperature of the flame envelope.  
 $T_S$  = , , , , slag surface.

It is also proportional to the emissivity of the flame envelope; the more luminous the flame the higher will be the emissivity. Hence, for the highest transfer of heat by radiation a hot luminous flame is essential.

In the case of heat transferred by convection from the flame to the charge, if the flame does not touch the charge there will be no heat transfer.

Owing to the high conductivity of steel scrap, the charge is able in the initial stages to absorb considerable quantities of heat, largely by conduction from the flame. The quantity of heat which can be absorbed depends, apart from the flame temperature, on the nature and conductivity of the scrap mass. Ordinary heavy steel scrap is the most efficient heat absorber; light scrap such as turnings and shearings possesses too many insulating air spaces; very heavy mill scrap must be thoroughly heated throughout the whole mass before melting takes place, except on the edges and corners. Owing to this considerable withdrawal of heat from the flame, its temperature is lowered, which results in slower melting if the heat input is not stepped up to balance the loss. The furnace heat input therefore should be at a maximum at this stage of the charge; it is probably correct to say that at this period the only limiting factor to the amount of heat that can be delivered to the charge is the ability of the furnace to burn in the proper place all the gas that can be supplied to it.

That melting the charge is performed largely by convection is evidenced by the high rate of melting achieved by a non-luminous

coke-oven-gas flame as in the Hoesch furnace; the intrinsic temperature of such a flame is higher actually than that of a luminous flame from producer or mixed gases.

After the addition of hot metal or the melting of cold pig, the chemical process starts along with the completion of the physical process. Reactions commence between the silicon, phosphorus and manganese of the iron and the oxide of iron formed during melting. These reactions are exothermic, so that an additional inside source of heat is provided, which, together with carburisation of the scrap by the carbon of the iron, raises the speed of melting. A point is reached when all the solid material is submerged under the slag, and from this point on the temperature of the charge increases more slowly, owing to the slower conduction of heat through the slag layer and the progressive exhaustion of the silicon, phosphorus and manganese in the hot metal. The temperature of the furnace itself now rises, owing to reflection of heat from the slag surface and decreased absorption, and this high temperature must be maintained in order to drive down the necessary heat for the clear melting of the charge and to make good the increased losses due to radiation. As the melting of the charge nears completion, the flame may be said to have practically fulfilled its active rôle, and now becomes more passive. The term "*more* passive" is used because, even during refining, the furnace atmosphere has its own influence on the speed of the reactions. This, however, is not due so much to its temperature as to the effect of the products of combustion on the transfer of oxygen through the slag to the metal.

Given a hot enough flame, melting can be speedily accomplished with or without luminosity, provided that the flame is well down on the charge. With a coke-oven-gas flame the temperature is sufficiently high to melt fast without any preheat; the flame temperature then depends to a great extent on the air preheat and varies with it. In the case of mixed gases of from 200 to 230 B.Th.U. per cu. ft., the flame temperature is not high enough to melt quickly without considerable preheat. It has been observed and commented upon several times by furnace operators that the mixed-gas flame must possess luminosity in order to melt fast. Here the flame melts fast because it is hot, not because it is luminous; the luminosity merely indicates that the preheat has been high, and this, with or without luminosity, produces a hot flame. To maintain this :

- (a) The gas and air preheats should be around 1200° C.
- (b) The gas velocity should be high.

If these two factors are unfulfilled, the melting power of the furnace falls off and production is lowered.

In particular, where the flame temperatures are low owing to inadequate preheat of the air and gas, luminosity becomes a factor of major importance in promoting the transfer of heat. In a recent

admirable paper, Fisher,<sup>(1)</sup> of the Bethlehem Steel Corporation, has shown how the total radiation of the open-hearth flame can be measured and recorded, and, further, has demonstrated that the output of the furnace in tons per hour depends to a very great extent on the flame radiation as measured by him. The above two factors also apply to other heating gases such as producer gas, but from the point of view of furnace design the problems are easier, because the compromise between ingoing and outgoing port velocities is less important than with the higher-calorific mixtures, notably mixed coke-oven and blast-furnace gases.

#### REFINING WITH A NON-LUMINOUS FLAME.

Refining can be carried out without luminosity, but to a very limited extent only. The Hoesch furnace, without artificial luminosity, will refine fast, but only if care is taken that the charge does not melt out hard.\* If it does, and as a result receives heavy feeding, the slag will quickly come up in a foam. The effects of a foaming slag can be disastrous to the brickwork, particularly the roof; once it has started there appears to be very little that can be done to suppress it. The only remedy is immediately to cut down the gas in order to preserve the brickwork, and keep on feeding oxide gently. The charge will, however, gradually lose heat, and the refining time be considerably prolonged, and in addition the furnace will probably be damaged.

The same thing happens, but to a greater extent, when ore is charged and the proportion of iron increased; actually it is impossible to do this with a non-luminous flame, as the resulting foam is uncontrollable.

A non-luminous-gas furnace is therefore inflexible, because in order to prevent foaming :

- (1) It cannot work with varying proportions of scrap and hot metal.
- (2) The charge must be melted out with not more than 0·4-0·5% of carbon and even then it must be treated gently.
- (3) Fluorspar, as an aid in fluxing the slag, can be used only sparingly. Bauxite, when available, can be used as a substitute.

#### THE NATURE OF SLAG FOAMS.

The causes and nature of slag foams are not easy to analyse. Foaming slags are always bulky, so that they rise considerably above the normal slag level in the furnace. In appearance the surface of the slag has a "shimmering" effect, which is caused by the breaking of large numbers of very small bubbles of gas. The surface of the slag also is uneven and gives one the impression that

\* That is, with a high carbon content.

it is not properly liquid. Foaming is accompanied by a slight "sizzling" noise, due to the continual collapse of the bubble skins; this can be clearly heard and the state of the slag foretold even with all doors down.

The slag in these cases is composed, in the upper layers at least, of large numbers of small bubbles, which are rising slowly to meet the gas, but not through a medium; they are rising bodily, the bubbles touching each other side to side, above and beneath. Why are the bubbles so small compared with those in a normal slag? The probable answer is that even with normal slags the bubbles arising from the slag-metal interface are also small, but in these cases, owing to the considerably lower surface tension of the slag, they quickly coalesce, becoming reduced in number and increased in size; they rise quickly and burst easily, leaving a liquid slag into which the following bubble will rise and burst. As long as it bursts before its successor reaches the surface, a non-foaming slag is the result. Assume for a moment that, owing to high surface tension, the bubble does not burst immediately. The succeeding bubble comes to the surface and lifts the first one clear of the surface before it bursts. If the top one even then does not burst, there may be several bubbles one above the other, all in contact, the whole lot being continually lifted by those underneath. The bubbles cannot be pushed out sideways, because the same thing is happening all over the bath; the result is a foaming slag. If a furrow is cut in the slag, e.g., if the walls of the slag bubbles are forcibly burst by the introduction of a rod, by throwing in scale or by any other addition, the bubbles can then displace themselves sideways into the furrow, and the slag for a short time appears to flow into the furrow. This is a temporary phase only and the foaming is soon resumed.

It is noticeable that as the carbon drops to 0·2–0·3% the foam recedes, the slag resuming its normal character. This may be due to the retardation of bubble formation, so that individual bubbles have time to reach the surface and burst before the arrival of their successors. It is probably due also to decreased surface tension, owing to the changed composition of the slag as the carbon content of the steel drops. Samples of foaming slags show wide variations in composition, though it does appear that foaming is generally associated with high iron or high silica contents of the slag.

Foams such as these are rarely encountered in producer-gas-fired furnaces, which can be worked with 100% iron if necessary without serious trouble. It is true that in such cases considerable "swelling" of the charge takes place, owing to the large content of gas bubbles in both the metal and the slag resulting from the intense reactions of the oxide underneath, but the slags are not truly foaming. True foaming will set in during reversal, when the gas is off the furnace for a short period. Also in the case of coke-oven-gas furnaces, provided that atomised tar, oil or pitch

to the extent of approximately one-third of the total heat input is injected with the flame, almost any percentage of iron can be carried; in this type of furnace, when the charge is on the "ore boil," if all the tar is turned off, the slag will quickly rise to a foam. If the tar is reintroduced the flame will cut a large groove through the slag; the high slag on each side of the groove falls into it, and the slag as a whole rapidly flows towards it, so that in a few moments the slag has reverted to its normal state.

Flame luminosity therefore definitely inhibits foaming; whether it is artificially introduced by tar or is naturally present as with producer gas, the effect is the same. The degree of foaming does depend on the degree of "actual" luminosity, because in the case of mixed gases, although a flame may appear to the eye to be dazzling white, yet a foam will result if too much iron is used, which indicates that "actual luminosity" is not the same as "apparent."

Even with producer-gas flames, if the port is so badly worn that that gas is not travelling down on the bath, foaming will be induced, and this applies to a greater degree to mixed gases. The question of flame direction therefore also is important.

#### EFFECT OF LUMINOSITY ON SLAG FOAMS.

Owing to the fact that foams immediately react to changes in luminosity, it must be inferred that slag composition is not of great importance in this respect. It might be argued, however, that the furnace pressure has some effect on foam, owing to the fact that slags will foam in producer-gas furnaces at the moment of reversal, and it may well be that in mixed-gas furnaces, with lower gas volume inputs and straight-through valves, the furnace pressure is on an average lower than in producer-gas-fired furnaces. However, increased furnace pressure will not decrease a foam once started, and actually it is not easy to understand how the pressure can affect the slag surface tension. One has to face the fact that a mixed-gas furnace may have a slag exactly similar in composition to that in a producer-gas-fired furnace, with the bath compositions in both cases similar, yet in the former case the slag foams and in the latter case it does not.

Considering all the evidence, it must be accepted that flame luminosity is the governing factor—not the "apparent" but the "actual."

As slag is a poor heat conductor and metal a good conductor, it is probable in the case of a non-luminous flame, which supplies its heat by convection, that the lower layers of slag give up heat to the metal more quickly than they receive it from above. Thus, while the top surface is comparatively hot, the reverse is the case at the slag-metal interface.

At or through this cold interface bubbles are formed or pass; as their formation is accelerated, the slag becomes more bulky

and the conductivity less, so that the bottom surface becomes colder still. The slag, being colder, has a greater surface tension, and a foam results in the manner previously explained.

The effect of a luminous flame on the bubble walls may be likened to the effect of the radiant heat of the sun passing through the glass of a greenhouse. The heat drives into the greenhouse and concentrates there. So, it is considered, has the radiant heat of a luminous flame the property of driving heat down through the bubble walls deep into the slag; thus, by its heating effect alone it decreases the surface tension, causing the bubbles to burst easily. As soon as luminosity disappears, the "penetrative heat," with its effect on surface tension, disappears. It is also quite possible that such penetrative heat is the result of a more penetrating force than light, *e.g.*, ultra-violet rays, which may explain the difference between "apparent" and "real" luminosity. Such rays are known to possess considerable disintegrating effects and powerful influences on chemical action; such effects may be exercised on the surface tension of the bubble walls.

Ellefson and Taylor<sup>(2)</sup> have shown that the surface tension of a fused salt varies almost instantaneously with a change in the atmosphere around it. For instance, in making a small melt of lithium metaborate in a platinum crucible in a gas-fired furnace, it was possible for the melt to spread over the entire crucible bottom or to gather into a drop according to whether the combustion conditions were oxidising or reducing. This example is striking because of the rapid change of the surface energy with change in combustion conditions.

This effect is interesting in connection with foaming slags, where the surface energies also may alter with a change in atmosphere.

#### EFFECT OF FOAMING SLAGS ON REFINING.

Foaming slags are, by their very nature, excellent insulators. The top surface becomes very hot, and by intense reflection throws the heat back up at the roof, causing it to warm up quickly and melt. Also, owing to decreased absorption of heat by the charge, more heat is thrown on to the outgoing ports and regenerators, the temperature of the latter rising steeply. This effect is more pronounced on new than on old roofs, owing probably to the greater conductivity of an old roof. Further, it is not easy to stop the roof "running"; unless the gas is practically all shut off, the running will continue in a lesser degree.

With the gas considerably slackened down, the foam still persists; as a result the steel charge becomes chilled, the slag becomes deficient in iron and the steel high in phosphorus, both being cold. Further time has to be expended to get heat back into the charge and the slag into condition; the roof has probably been damaged,

and in general it is a trying time for furnace personnel, who get impatient and over-anxious to tap.

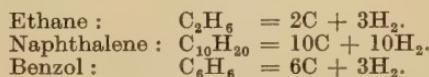
#### LUMINOSITY IN MIXED-GAS FLAMES.

Clean blast-furnace gas burns with a non-luminous flame, as also does normally produced coke-oven gas without preheat. If heated above approximately 900° C., certain changes take place. Methane is decomposed as follows :



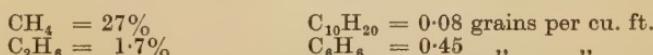
the carbon being released as extremely fine particles, which burn quickly to give rise to luminosity.

In addition, the heavy hydrocarbons ethane, naphthalene and benzol contribute their quotas of finely divided carbon, as follows :



The decomposition of the above gases takes place over the same range of temperature approximately as methane.

In a furnace using, say, 60,000 cu. ft. per hr. of coke-oven gas of the following composition :



the amounts of carbon shown in Table I. are yielded on complete decomposition.

It will be noted that although ethane constitutes only 1.7% of the volume of the gas, it yields, by virtue of the greater amount of carbon in its molecule, 11.05% of the total precipitated carbon.

The luminosity of a mixed-gas flame depends entirely on the above constituents, so that variations in particular of the methane and ethane will vitally affect the furnace working.

TABLE I.—*Carbon Yielded on Complete Decomposition of Hydrocarbons in Coke-Oven Gas.*

60,000 cu. ft. of gas per hr. containing : CH<sub>4</sub>, 27%; C<sub>2</sub>H<sub>6</sub>, 1.7%; C<sub>10</sub>H<sub>20</sub>, 0.08 grains per cu. ft.; C<sub>6</sub>H<sub>6</sub>, 0.45 grains per cu. ft.

Constituent.	Total Carbon. Lb. per hr.	Proportion of Carbon from each Source. %.
Methane . . . .	541.2	88.26
Ethane . . . .	67.8	11.05
Naphthalene . . . .	0.586	0.095
Benzol . . . .	3.7	0.586
TOTAL . . . .	613.28	99.99

There is evidence, noted by Wesemann,<sup>(3)</sup> that the luminosities produced by carbon atoms from different sources are not equal. This appears to depend on the fineness of separation of the carbon, the greatest luminosity being derived from carbon which is precipitated in a very fine state of subdivision. It may be inferred, therefore, that the 613 lb. deposited as shown in Table I. will give rise to greater luminosity than that produced by the atomisation of 75 gal. of tar, for instance. In the latter case no atomic precipitation takes place; the tar is merely disrupted by pounding with steam or air into small globules, each probably consisting of thousands of molecules, which is relatively an extremely coarse precipitation.

It appears that the carbon derived from naphthalene and benzol, in particular, gives rise to very high luminosities, which may be due to these more complex molecules breaking down at lower temperatures than methane.

The actual degree of fineness of the carbon derived from these various sources on precipitation is not known, but the carbon in general in a "cracked" coke-oven gas is to a great extent visible to the naked eye, and can be seen deposited on the sides of a glass tube if the hot gas is aspirated through it. This shows that if the carbon is in the first place precipitated in an atomic state, the atoms must soon coagulate into discrete particles which are big enough to be visible in bulk. Rummel and Veh<sup>(4)</sup> have shown that when hydrocarbons are cracked by heat, the reaction probably takes place in two stages. At lower temperatures tars and light oils are formed; at higher temperatures carbon skeletons are left, owing to the gradual breaking away of hydrogen atoms. During combustion hydrogen burns first, thus bringing up the carbon aggregates to a white luminosity.

According to Cantelo<sup>(5)</sup> the percentage dissociation of methane at various temperatures is as shown in Table II. While a deposition of carbon is shown here as low as 500° C., it is certain that

TABLE II.—*Dissociation of Methane at Various Temperatures.*

Temperature. °C.	Composition of Equilibrium Mixture.	
	CH <sub>4</sub> . %.	H <sub>2</sub> . %.
500	63.9	36.1
600	37.9	62.1
700	16.3	83.7
750	13.0	87.0
800	7.5	92.5
850	4.5	95.5
900	3.6	96.1
1000	2.0	98.0
1100	0.8	99.2

there is no luminosity in the flame in the furnace below 950° C., which indicates that the bulk of the carbon precipitated up to this temperature may be deposited on the regenerator brickwork, so that none, or very little, reaches the flame, or that these amounts of carbon are completely consumed by the water-gas reaction (see below).

Simmersbach,<sup>(6)</sup> in an older research, has shown that coke-oven gas definitely loses in calorific value as the preheat is increased, as follows :

Temperature of preheat. ° C.	0	800	900	1000	1100	1200
Loss of calorific power. %		4	13	18	22	33

This loss he puts down to the decomposition of methane and heavy hydrocarbons ; the theory is not explained.

Considering the decomposition of methane :



if 16 lb. of methane are burnt with oxygen, they produce slightly less heat than do 12 lb. of carbon and 4 lb. of hydrogen, the difference being due to the heat of decomposition of methane. But one volume of methane produces two volumes of hydrogen, so the calorific value per unit volume is considerably lower. This is the result that would be produced by taking samples of the gas before and after preheating and calculating the calorific value per cubic foot from the analysis. In considering an open-hearth system, however, while it is true that the calorific value is reduced per cubic foot, nevertheless the double volume of gas resulting from the decomposition is pushed through the gas port, so that the total heat received by the furnace is the same.

If the theory that carbon is deposited in the checker work and does not reach the port at all is correct, this would account for Simmersbach's statement. In this case, when the furnace is reversed the carbon will burn away in the waste gas, yielding its heat to waste. Quite possibly the degree of fineness of the precipitated carbon would affect the proportions retained by the brickwork and passed on to the flame, which may account for Wesemann's theory that the luminosity of the gas appears to vary with the fineness of subdivision of the precipitated carbon ; in other words, if the carbon is deposited coarsely instead of finely, more may cling to the brick surfaces and thus less reach the flame, which then appears less luminous.

Hermanns<sup>(7)</sup> goes so far as to say that, owing to this loss of calorific value in coke-oven gas by heating, the regeneration of pure coke-oven gas is out of the question, and that considerable loss of calorific value in early trials of mixed-gas operation due to this effect were noted.

This raises the interesting question as to whether the regeneration of a coke-oven/blast-furnace-gas mixture is in fact the most economic and efficient way of utilising the coke-oven gas. An alternative method which suggests itself is to regenerate the blast-furnace gas only in smaller regenerators; the coke-oven gas can be introduced cold through water-cooled burners either at the back of the gas port, where it would be injected into the hot blast-furnace gas, or direct into the furnace above the gas port. The resulting non-luminous gas could be rendered luminous by the introduction of tar through the coke-oven-gas burner. This method would possess at least the following advantages :

- (1) The total calorific heat of the coke-oven gas would be delivered to the furnace.
- (2) Losses of coke-oven gas past leaking dampers would be eliminated.
- (3) Thermal losses due to the endothermic nature of the cracking of the hydrocarbons would be eliminated.

One factor which has a great effect on the luminosity of mixed-gas flames is the moisture content of the mixture. This gives rise to the water-gas reaction :



in which the carbon precipitated by dissociation of the hydrocarbons is eliminated by interaction with water vapour. While the carbon is precipitated apparently at 950–1150° C., the water-gas reaction reaches its maximum intensity at 1200–1250° C., but proceeds also at lower temperatures.

Table I. shows how 613 lb. of carbon per hr. are precipitated from the complete dissociation of 60,000 cu. ft. per hr. of coke-oven gas. If, in mixed-gas operation, this is mixed with 120,000 cu. ft. per hr. of blast-furnace gas, and if, as was determined in an actual test, the coke-oven gas enters the valves at 23° C. and the blast-furnace gas at 18° C., it can be shown that the blast-furnace gas brings in 2448 cu. ft. of water vapour per hr. and the coke-oven gas 1662 cu. ft., making a total for the mixed gases of 4110 cu. ft. of water vapour per hr.

Calculations show that the weight of carbon required to combine with the oxygen of 4110 cu. ft. of water vapour is 84.5 lb., so that the 613 lb. of carbon precipitated in this case is decreased by 84.5 lb. or 13.77%, owing to the presence of these amounts of water vapour. If the blast-furnace gas entered the valve at 40° C., the greater amount of moisture carried would be sufficient completely to eliminate the whole 613 lb. of carbon, the result being complete lack of luminosity. In practice it is unlikely that all the water vapour is decomposed, owing to the temperatures of preheat not being high enough, but there is here the source of a considerable loss of luminosity.

The cure is to cool the gases as far as possible before entry.

This is doubly important where the proportion of methane and higher hydrocarbons is already low, and where probably high checker temperatures are carried to extract the "last ounce" of luminosity out of an already lean gas; the furnace reactions are more sensitive to variations with low than with high luminosity.

Another important point is that no water should be allowed to leak on to any part of the culverts or regenerator brickwork. At the average culvert temperature, the dew-point of the gas is high, so that large amounts of moisture can be carried in.

Where liquid fuels such as tar are used as "carburetters," these reactions suggest that compressed air would be a greater asset than steam as the atomiser.

#### MIXED-GAS PRACTICE AND FURNACE DESIGN.

Normally, mixed gases are regenerated and injected into the furnace through ports of conventional design. Furnaces designed to use producer gas which are converted to use mixed gases must have the gas ports decreased in area if adequate velocity is to be maintained, owing to the use of a 220-230 B.Th.U. gas as opposed to 140-150 B.Th.U. for producer gas. On the suction end, the smaller port has to pass considerably greater volumes of waste gas through in order to warm the checkerwork up to "cracking" point, a temperature normally higher than that required with producer gas, and, it must be borne in mind, with a cold gas entering the regenerator on reversal instead of hot producer gas. All this means that the suction on the gas port must be much higher with mixed-gas than with producer-gas practice, and this is generally achieved by an auxiliary damper placed in the air return and sometimes by decreasing the air port area as well. With the greater suction on the gas system more air infiltration takes place, a most prolific source of loss of heat efficiency in mixed-gas practice.

The size of the gas port is a key item in the design of mixed-gas furnaces. If it is too small, it is impossible to preheat the gases sufficiently, owing to the very great cooling effect on the checkers of the infiltrated air. In such a case the auxiliary damper may be progressively lowered, until a point is reached at which the gas checker temperatures actually decrease, owing to the greater cooling effect of these air leaks; needless to say, at this point the total draught on the furnace decreases and the furnace pressure itself rises.

Also, with a small gas port the pressure in the gas system when "on gas" is so high that large amounts of gas leak through the brick-work crevices, particularly on the uptakes, which is dangerous where blast-furnace gas is concerned; larger amounts also will leak past damper-type valves, an amount that is increased by the higher suction behind them. Further, any advantage which it might be hoped would accrue from the higher ingoing velocity of the gas is lost owing to the lower preheat of the gas.

If the gas port is too large, higher preheats can be achieved without high suctions and pressures and therefore with less leakages. From the thermal efficiency standpoint this is far more desirable, but a low ingoing velocity, with low flame temperature development and rapid wear on the roof, is the result.

In an open-hearth furnace the drop in pressure or draught through the flues, checkers, uptakes and ports due to friction with the encountered surfaces is almost negligible compared with the great loss due to the frequent changes in direction of the stream, often greater than a right angle. In order to reduce to a minimum the ultimate or chimney draught required to pull a given volume of waste gas out, the passages and uptakes should, wherever possible, be streamlined and the changes in direction curved. This will result in less air infiltration and less gas loss.

The regenerators and, if possible, the uptakes should be encased to prevent leaking brickwork, but insulation should be considered with caution. All uptakes should be of ample dimensions.

From the above considerations, straight-through damper-type valves are most desirable, but they undoubtedly leak considerable quantities of gas to the chimney, particularly when the slope is such that the bottom of the damper is nearest to the chimney. If the slope is the other way, gas is liable to leak up through the apertures in the chase through which the stem and water-cooling pipes pass and foul the valve-house atmosphere. In either case the damper-seat interface must be a machined fit.

It is considered that a water-seal reversing valve of the Forter type would be more satisfactory if used carefully and with proper design, although the "streamline" effects have to be somewhat sacrificed. Nevertheless, leakage to the chimney is completely prevented, so that, if the seal is deep enough, higher draughts can be carried without fear, as also can higher gas pressures.

#### PORT COOLING.

Owing to the high exit velocity of the waste gases through the gas port, considerable erosion of the nose of the port takes place. This necessitates water-cooling, of which there are several types in use. The conventional water tubes forming the inside surface of the port have been found effective. If eight  $1\frac{1}{2}$ -in. pipes are spaced 1 in. apart, a total length of cooling of 19 in. is secured, which is sufficient for most purposes. In this case the inlets are at the front of the furnace, and the water tube runs in, up and over the inside of the gas port and down the other side. The tube is then extended for approximately 9 in. towards the back, where it is doubled back and lies side by side with its ingoing half; the outlet then comes out by the inlet and two cooling pipes are provided from one inlet, four of which would be required for eight cooling pipes. These pipes have the advantage that, as the floor of the air port wears

back, fresh refractory cement can be put on the pipes to restore the block contours. The gas port behind the 19 in. of cooling does tend to widen out, particularly if combustion is not complete in the furnace. To secure cooling of the whole length of the gas port, tank types such as the Blair port can be considered, but here, if the port is long, considerable cooling of the ingoing live gas and of the exit waste gas is to be expected, in spite of the thin brick lining employed in such ports.

#### PORT VELOCITY AND SLOPE.

Owing to the low total mass of solids in mixed gases, it is very necessary that the gas should be injected with a higher velocity than is the case with producer gas; owing also to the low density of the gas, it should be projected into the furnace more steeply. A minimum velocity of 80 ft. per sec. and a port inclination of approximately one in five should be aimed at; the roof of the air port should be more steeply inclined than in the case of producer-gas operation.

A mixture of 60,000 cu. ft. of coke-oven gas and 120,000 cu. ft. per hr. of blast-furnace gas heated to 1100° C. and passed through a port 20 in. × 22 in. will give a velocity of approximately 80 ft. per sec. into the furnace with a mixed-gas pressure of about 0·4 in. W.G. If higher velocities than this are sought, while in themselves advantageous, considerably greater leakages are likely to ensue, with resulting losses in thermal efficiency.

As a very rough guide to the flexibility of mixed-gas furnaces without artificially produced luminosity, it may be stated that, given the following conditions :

Heavy hydrocarbons in the gas . . . . .	1·5-2·0%
Naphthalene plus benzol . . . . .	0·5 grain per cu. ft.
Maximum temp. of coke-oven gas entering valves . . . . .	21° C.
Maximum temp. of blast-furnace gas entering valves . . . . .	18° C.
Average checker temp. between highest and lowest at reversal . . . . .	1100° C.
Proportion of blast-furnace to coke-oven gas. . . . .	2 : 1
Approximate hot-metal analysis :	
Silicon . . . . .	0·3-0·4%
Phosphorus . . . . .	1·2-1·4%
Manganese . . . . .	1·0-1·2%

the maximum proportions of iron which can conveniently be carried in fixed furnaces with varying percentages of methane in the gas are as follows :

Methane. % . . . .	26-28	28-30	30-32	Over 32
Max. iron. % . . . .	40-50	50-60	60-80	Up to 100

Fixed furnaces which have slagging facilities will carry higher proportions. Also where all-cold charges are worked slightly

higher proportions can be used. Grey and "kishy" iron will reduce the proportion, whilst low-silicon irons will increase it. With very low water-vapour content and high checker temperatures the proportion may be increased by 10%. Higher naphthalene and benzol contents in the gas will also increase it. Nevertheless, if, owing to variation in scrap or metal quality, the charge melts out hard and has to be heavily fed, even with the above limits of hot metal bad foaming is likely to start, so that for safety's sake the amounts used are usually lower than the above maxima. In all cases it is assumed that the flame is well down on the bath and that complete combustion takes place.

In order to overcome the need of attaining the high gas-checker temperatures, with consequent port erosion, air infiltration and gas leakage, required to obtain luminosity, it is strongly recommended that in all mixed-gas furnaces a second source of luminosity be provided.

#### ARTIFICIAL LUMINOSITY.

The introduction of tar or pitch, atomised by steam or compressed air, will provide artificial luminosity. It can be used in several ways; in most cases it is atomised with steam and delivered to the furnace through a water-cooled "gun." This may be introduced at the back of the gas port where the tar is injected directly into the gas mixture on its way to the mouth of the port. This ensures good admixture, but has the disadvantage that the atomised stream is out of sight, also that difficulties are involved when it is necessary to scrape the floor of the port from the back. To get over this difficulty, the gun has been introduced through the side of the gas port, the jet then turning through a right angle to face the port opening. Here, again, the tar jet cannot be seen.

Another method which has given great promise is to lay a longer gun down the floor of the air port, so that the nose reaches to the entrance of the gas port but is slightly above it. The tar stream then has the advantage of burning in pure preheated air and of being projected well down on the bath, through and in admixture with the gas stream. On occasions when the gas supply has failed, charges have been melted, refined and tapped with tar alone, injected in this manner.

The tar should be heated to 80-90° C. and arrive at the injector at not less than 40 lb. per sq. in. pressure. The steam used should be dry and at approximately 80-90 lb. per sq. in. pressure: figures for temperature and pressure vary according to the type of gun used. Also, the tar should be cleaned in some sort of strainer before being pumped round the plant. When it is desired to restrict the quantity delivered to any furnace, it is preferable to slow down the pump and thus reduce the pressure, rather than to rely on closing valves, which, unless of special construction, tend

to become clogged up in the very small apertures used, so that the flow will suddenly cease.

Most efficient atomisation is probably achieved by pressure alone, but the difficulties of using a water-cooled pressure atomiser with mixed gases are considerable.

#### AIR REQUIREMENTS.

It is of the utmost importance that plenty of air is delivered to the furnace. Even if air is blown and measured in quantity, constant check analyses should be done on the waste gases, which should contain approximately 4% of oxygen. The sample of waste gas should be taken well inside the gas port, so as to avoid interference from air infiltration. If unburnt gases are allowed to reach the exhaust end, rapid wear of the ports, back stoppings and uptakes will take place. Blown air has particular advantages towards the end of a campaign, when the air checkerwork is becoming clogged. With clean checkers of normal aperture the air naturally induced should be quite sufficient.

While exact regenerator dimensions for use with mixed gases cannot be laid down, it can be stated that the drop on reversal in the gas and air checker temperatures should not exceed 200° C. If the range is greater than this, larger checker volume is required; this should be provided by an increase in height rather than in width or length.

#### FURNACE STRUCTURE.

Sloping back walls, apart from their usual advantages, have been noticed to benefit the roof life: in a shop which has furnaces with straight and sloping back walls, the latter have given considerably greater roof lives, owing, it is thought, to the heat intensity of the flame being spread over a greater area.

It is considered most important that the roof should not be too low over the bath. With correct gas-port design, a roof which has given a good life on producer gas should give a good, if slightly shorter life, on mixed gases. This is attributed to the difficulty of preserving the flame direction throughout its travel over the bath, owing to the greater buoyancy and to the effect of hydrogen and moisture on the silica, though some silica bricks stand up better to this condition than others. The greater tendency to foaming has a bearing also on roof wear. The lower the roof over the bath the faster the furnace will work and the lower will be the heat consumption, but the risks are great, and short lives may be the result.

#### MIXED-GAS OPERATION.

The operation of mixed-gas furnaces depends to a far greater extent on instruments than is the case with producer-gas furnaces. Normally in the latter case the instrument panel will consist of :

- (1) Draught indicator and recorder.
- (2) Air flow indicator (if blown air is used).
- (3) Gas pressure recorder between valves and regenerators.
- (4) Possibly air checker temperature recorders.

In the case of mixed gases, with injected tar, the panel will contain the following :

- (1) Draught indicator and recorder.
- (2) Blast-furnace gas pressure indicator.
- (3) Blast-furnace gas flow indicator and recorder.
- (4) Coke-oven gas pressure indicator.
- (5) Coke-oven gas flow indicator and recorder.
- (6) Air flow indicator.
- (7) Temperature recorders on both gas checkers.
- (8) Temperature recorders on both air checkers.
- (9) Tar temperature recorder.
- (10) Tar pressure recorder.
- (11) Tar flow recorder.
- (12) Steam atomisation pressure.
- (13) Mixed-gas pressure indicator.
- (14) Furnace pressure indicator and recorder.

It is evident, therefore, that a melter who has spent his life on producer-gas furnaces has considerably to increase the scope of his knowledge when introduced to mixed gases.

Furnaces are normally worked by setting the blast-furnace gas at a constant value and varying the heat input by altering the flow of the coke-oven gas. In a plant working without blast-furnace gas-holders, the blast-furnace gas flow is likely to vary considerably with the pressure, this being dependent on the number of blast-furnaces in operation. This variation affects the process to an extent not generally recognised, as the blast-furnace gas determines the velocity of the ingoing gases. If the flow is set at 120,000 cu. ft. per hr. and then varies from 90,000 to 150,000 cu. ft., depending on the gas-main pressure, the variations in calorific input, flame velocity, temperature and direction are pronounced. Likewise, variations in the coke-oven gas pressure are even more disturbing; instances have been noted of a first hand setting his coke-oven gas flow at 50,000 cu. ft. per hr. which the furnace could well stand; he then goes off with his colleagues to help fettle another furnace and as soon as his back is turned the main pressure increases, his coke-oven gas flow rises to 70,000 cu. ft. per hr. and he returns to find part of the roof a mass of "icicles."

With regard to items (7) and (8) above, the radiation pyrometers should be sighted on to the top of the checkerwork adjacent to the bridge. In this connection it may be mentioned that the same air and gas preheats have been found with widely differing regenerator capacities, which, it has recently been pointed out, are due to the considerable regenerative potentials of the slag pockets and uptakes.

Items Nos. (9) to (12) govern the correct atomisation of tar, and are important where the tar gun is out of sight. No. (13) will give very good indications, when a furnace becomes sluggish, of where the trouble lies.

No. (14) is considered to be of the utmost value, particularly in plants where the chimney damper or boiler fan are easy and handy to manipulate. If intelligently used it will pay large dividends. A suction in the furnace—with consequent air intake through the doors, its effect on flame direction and on the checker temperatures, and also the implication that the gas or air delivery is insufficient—is as prolific a cause of loss of production as a comparatively high pressure, with consequent general wear on the furnace and implications that the checkers are obstructed or the valves are not operating properly. The furnace should work best with a pressure of approximately +2 mm. W.G., and the draught conditions should be adjusted to give this. Finally, a calorimeter such as the "Sigma" and temperature indicators in the blast-furnace and coke-oven gas mains entering the shop are considered indispensable.

#### MIXED GASES AND DOLOMITE CONSUMPTION.

Experience has shown that dolomite consumption is lower with mixed gases than it is with producer-gas practice, and on an average less bottom trouble is experienced.

On one furnace which had a new bottom installed at the time of conversion to mixed gas, notes of fettling times and dolomite consumptions were kept for a nine-week period after the furnace had worked 27 weeks. For this nine weeks the average fettling time was 39 min. per charge, including all "bad-bottom" time; the dolomite consumption was 51.5 lb. per ton of ingots; the roof life incidentally was 36 weeks, without any patching.

It pays to use finer grades of dolomite or tarred dolomite for topping the banks, because, if foams are experienced, strength is needed at the sill levels. It has been found that the bottom tends to build up in the shape of a promontory in front of the gas port, and the difficulty often is to keep the bottom down to correct levels rather than to fettle it. In general, bank erosion is about the same for mixed-gas and producer-gas practice, but the bottom requires less dolomite in the former case.

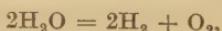
#### METALLURGICAL CONSIDERATIONS.

It is found that mixed gases without tar addition appear to have a less oxidising effect on the bath than producer gas, even though there may be the same percentage of oxygen in the waste gases in both cases. For instance, mixed-gas furnaces run on a lower proportion of iron in the charge; an 80-ton charge will take, say, 24 tons of iron without charging oxide, while with an exactly

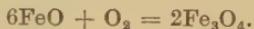
similar charge a producer-gas-fired furnace will take 30-32 tons to melt out at the same carbon content. Also it is found that the percentage loss of manganese after the ferro-manganese addition to the bath is, on an average, less with mixed gases, so that less ferro-manganese is required to bring up the bath manganese to the desired point.

Further, it has been noted that slag-metal equilibrium is reached more quickly under a mixed-gas flame, so that it is possible to run the carbon very low with less iron (total) in the slag. A heavy addition of scale to the charge will run the carbon down rapidly, but as soon as the feed is exhausted the bath appears to reach a dead-melted condition quickly, even at low carbon contents; this necessitates greater care to prevent rephosphorisation, to which there is a distinctly greater tendency than in producer-fired furnaces.

All this is probably due to the higher percentage of hydrogen or of water vapour in the furnace atmosphere. If at the highest temperature of the flame water vapour is dissociated thus :



it is possible that the oxygen would show itself as free oxygen when the waste gas was analysed, in which case combustion in the furnace would be judged complete, though at the same time free hydrogen was playing over the bath; free hydrogen will also be present from unburnt particles of the gas. At the face of the slag, where temperatures are considerably lower than at the highest-temperature parts of the flame, hydrogen may be able to recombine with oxygen and thus seize it before it is able to raise the slag  $\text{FeO}$  to  $\text{Fe}_3\text{O}_4$ , i.e. :



In this way the transference of oxygen through the slag to the bath is inhibited. Thus, oxidation oxygen has to be added more as oxide rather than as derived from the furnace oxidising atmosphere, and even after scale additions the oxidising effect appears to be more quickly neutralised, probably owing to the reducing effect of hydrogen. It is due to this that brisk boils are observed on mixed-gas baths only while oxide is working in the slag; when this is exhausted, the boil subsides and the slag looks stiffer, which is sometimes attributed to a "thickness" due to excess of lime.

Ferrous oxide in the slag may accumulate as oxide is added, the added  $\text{Fe}_3\text{O}_4$  giving up to hydrogen one atom of oxygen to become ferrous oxide, which is not further reduced, but also is not further oxidised as shown above. In this way the slag may have a reasonably high total iron which all exists as non-reactive ferrous oxide.

In a producer-gas furnace the slag's store of oxygen is constantly being replenished by the conversion of  $\text{FeO}$  to  $\text{Fe}_3\text{O}_4$  at the slag surface and in consequence possesses a quantity of total iron which is capable of exerting an oxidising effect at the slag-metal interface.

It is on account of this quick attainment of equilibrium that rephosphorisation has to be so carefully guarded against.

With very open slags, such as those low in lime, the oxidising and reducing reactions have far more scope to operate, owing to the greater freedom of the slags. Thus, when the carbon is dropping fast under an open slag which is freely boiling, lime is added to steady up the bath ; this checks the transfer of oxygen through the slag by slowing up the rate of presentation of FeO molecules to the surface of the slag for more oxygen. In this case whenever FeO particles do appear at the surface they are converted into oxygen carriers to the steel beneath ;  $\text{Fe}_3\text{O}_4$  molecules are unaffected.

Under mixed gases, however, the effect of increased lime is to prevent the  $\text{Fe}_3\text{O}_4$  molecules from appearing at the slag surface so often, and thus being reduced back to FeO :



In other words, under mixed gases it is not much good adding large quantities of oxide to a thin slag, owing to the probable high rate of  $\text{Fe}_3\text{O}_4$  reduction and loss of effective oxide at the slag surface.

#### CONCLUSION.

The conversion of a producer-gas-fired furnace plant to mixed-gas firing or to firing with cold coke-oven gas plus tar is generally carried out at the same time as increased quantities of coke-oven gas and clean blast-furnace gas are made available. If the coke-oven gas is rich in methane and heavy hydrocarbons, the regeneration of a blast-furnace/coke-oven-gas mixture is as efficient and economic, so far as steelmaking is concerned, as any other method of firing. Where, however, the coke-oven gas is lean, containing less than 27% of methane with a normal heavy hydrocarbon content, tar must be used as an artificial illuminant. The difficulties of efficiently introducing tar with mixed gases are considerably greater than when cold coke-oven gas plus tar are used, the difficulties being chiefly concerned in the shape of the gas port, which even in the case of producer-gas operation, is the major factor in determining the life of the furnace. The introduction of a mixture of cold coke-oven gas with tar as an illuminant is effected through a water-cooled burner ; the direction of the flame is constant, and there is no worry about the gas-checker temperatures, there being no gas regenerators.

In any plant where the amount of coke-oven and blast-furnace gas available becomes increased and, on the grounds of economy, the scrapping of the producer plant is considered together with the conversion of the open-hearth plant to firing with available gases, the question of the most efficient utilisation of the total gas surplus is one to which the most searching deliberation should be given.

Provided that the blast-furnace gas can be efficiently and eco-

nomically used in other spheres of heat requirement, the author is of the opinion that the best method of firing open-hearth furnaces is to use cold coke-oven gas and tar, tar oil or pitch, particularly where the very high metallurgical loads which have to be carried require tilting furnaces rather than fixed furnaces and where the coke-oven gas is likely to be of a lean nature.

An open-hearth operator who has confidence in the regularity of his heat input and resulting flame temperature is relieved of at least half of his normal troubles; he can then devote his time to the ultimate duty of every open-hearth manager, that of producing more, better and cheaper steel.

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[This paper was discussed jointly with the following one by A. H. Leckie on "The Study of the Thermal Performance of Open-Hearth Furnaces by the Correlation of Operating Data."]



# THE STUDY OF THE THERMAL PERFORMANCE OF OPEN-HEARTH FURNACES BY THE CORRELATION OF OPERATING DATA.\*

By A. H. LECKIE, Ph.D., F.I.C. (BRITISH IRON AND STEEL FEDERATION).

## SUMMARY.

A method is outlined for investigating the performance of open-hearth furnaces by the statistical examination of routine works records (provided that these include the measurement of the fuel gas). In Section I. it is shown how the appropriate correlation methods may be used to determine the optimum gas rate and air/gas ratio, and to investigate the effect of many variables in a quantitative way and the changes in thermal efficiency under various conditions. The methods are illustrated by examples taken from actual practice. Section II. is devoted to the discussion of simple methods of measuring and calculating the quantities involved.

## INTRODUCTION.

THE investigation of the thermal performance of open-hearth furnaces is usually carried out by constructing a heat balance on conventional lines. This may be done in two ways :

- (1) By determining experimentally and as accurately as possible all the quantities involved over a short period; and
- (2) by taking average figures of routine and less exact data from works records over a long period.

Examples of the first type of heat balance are given by Clements,<sup>(1)</sup> Kinney and McDermott<sup>(2)</sup> and Henry and McLoughlin.<sup>(3)</sup> Examples of the second type of heat balance are those of Rummel and Neumann<sup>(4)</sup> and of the Wärmestelle, Düsseldorf.<sup>(5)</sup> A combination of these two methods is recommended by the British Standards Institution,<sup>(6)</sup> which advocates the use of simple instruments over a period of a week or two.

The disadvantage of the first method of determining the heat balance is that it involves much laborious work with the installation of instruments and necessitates the presence of a large specialist staff of observers. For this reason measurements can only be taken over a short period—usually one or, at the most, a few heats. The result cannot therefore be considered to be representative, and on this account the method has been criticised, notably by Buell.<sup>(7)</sup>

\* Received October 1, 1943. A report to the Open-Hearth Committee of the Iron and Steel Industrial Research Council. The views expressed in it are the author's, and are not necessarily endorsed by the Committee as a body.

The objection to the second method is that, since accuracy is obtained by taking the mean of results over a long period of time, it is not possible to observe the effect of such day-to-day or week-by-week variations as occur, and much useful information is therefore missed.

The investigation of open-hearth furnace performance is always complicated by the large number of variables involved, many of which cannot be assessed in any quantitative way. Statistical methods, which have proved so successful in other fields of work such as agriculture and biometry, where large numbers of irregular variables are encountered, are therefore particularly applicable to the study of open-hearth problems. In Britain work of this kind has been carried out by the Open-Hearth Committee and published in two reports, one circulated privately in 1932 and the other reported in the Iron and Steel Institute Steelmaking Symposium held in 1938.<sup>(8)</sup> Abroad, the work of Buell in America<sup>(9)</sup> and of Bansen<sup>(10)</sup> and of Wesemann<sup>(11)</sup> in Germany may be mentioned. Such work, however, has chiefly consisted of the listing of a large amount of useful and comprehensive data on open-hearth practice and the preparation of graphical relationships, without any development of more elaborate statistical examination.

In the present paper a method is described by which much useful information on the effect of certain variables on the thermal performance of open-hearth furnaces may be determined from ordinary works records. It is assumed that the furnace is fitted with pyrometers which permit the gas and air preheat to be assessed. The only other essential instrument is a meter for measuring the fuel input to each individual furnace; whilst many furnaces in Britain are still without this, such installations are rapidly coming into use, and it is practically impossible to conduct serious investigations on furnace efficiency without a precise knowledge of the fuel input to individual furnaces.

#### *Variables Affecting Open-Hearth Furnace Performance.*

The principal variables affecting performance are indicated below, not necessarily in order of importance.

(a) *Design and Layout of the Furnace Passages.*—Obviously this has a great effect on performance, and one of the principal objects of thermal investigation is to eliminate other variables so that the effect of design is made clear.

(b) *Rate of Heat Supply.*—In general, the more heat that is put into a furnace the faster it works, but this implies that the heat is efficiently utilised and that sufficient, but not excessive, draught is employed.

(c) *Class and Character of Materials Charged.*—Certain materials are more difficult to melt than others; the differences between heavy and light scrap, the proportion of pig iron and the nature of the slag-

forming materials all have important effects well known to practical melters.

(d) *Nature of the Steel Made.*—This principally affects the refining time, though to a certain extent the type of material charged varies with the product, so affecting the melting period.

(e) *State of the Furnace.*—In some furnaces the effect of age shows itself by the choking of checkers and slag pockets. Others develop cracks and leaks interfering with heat input and draught conditions.

(f) *Mechanical Influences.*—Open-hearth performance also depends on mechanical factors such as crane capacity, provision for dealing with slag, staff and equipment for doing hot repairs, and many other factors of this nature. However, these are outside the scope of the investigation.

(g) *The "Human Factor."*—Although mentioned last, this is so important that the advantages of many technical improvements may be entirely obscured through this. For instance, in a shop where old slow-working furnaces are replaced by modern designs, perhaps with special features such as Venturi blocks, it may take several months before the melters learn the new methods of handling required, and the shop output may even fall during the transition period. In other cases the advantages of instruments may be lost through inadequately explaining their meaning to the men or through lack of maintenance. Such factors cannot, of course, be assessed quantitatively, but in several ways to be illustrated later the effect of psychological factors is very marked.

#### *The Definition of "Performance" and "Efficiency."*

As yet there is no satisfactory definition of these terms used in connection with open-hearth furnaces. The British Standards Institution Test Code<sup>(6)</sup> for these furnaces does not attempt definitions other than simple expressions of melting rate, heat consumption and heat consumption per ton of steel. The Open-Hearth Committee in its paper on "Open Hearth Data and their Correlation" presented to the 1938 Steelmaking Symposium,<sup>(8)</sup> combined output and thermal efficiency in a performance figure  $P$  defined as :

$$P = \frac{W}{VC} \text{ lb. per hr. per therm,}$$

where  $W$  = output in lb. per hr.,

$V$  = tapping capacity of the furnace in tons,

and  $C$  = heat consumption in therms per ton of steel output.

On this basis the figure 2 lb. per hr. per therm could be regarded as the line of demarcation between good and indifferent furnaces. Whilst this ratio is perhaps the best expression yet put forward for a general way of comparing performance, it still does not take into account many variables and is therefore likely to give a misleading picture occasionally.

Thermal efficiency, however defined, is not always a satisfactory means of expression, as the best thermal efficiency seldom coincides with maximum output figures, and from the economic point of view a furnace with very high thermal efficiency may not be giving as good results as one showing a lower efficiency figure and greater output. Also, it is well known that the apparent thermal efficiency of a furnace must depend on the proportion of cold metal charged and the relative proportion of time spent on melting and refining. This is illustrated in Table I., which summarises the results of several published heat balances.

TABLE I.—*Open-Hearth Heat Balances.*

	1.	2.	3.	4.	5.	6.	7.	8.
<i>Heat in = 100%.</i>								
Heat in fuel at furnace valve	72.6	} 100 {	87.7	90.1	95.4	98.9	94.0	91.8
Net heat of chemical reactions	27.4		12.3	9.9	4.6	1.1	6.0	8.2
<i>Heat out = 100%.</i>								
Heat in steel and slag = efficiency	19.1	16.2	15.8	27.8	18.1	27.2	18.0	25.2
Heat in waste gas to stack or boiler	51.6	61.0	43.2	42.8	41.0	45.8	41.6	43.2
Heat loss by radiation, &c.	29.3	7.3	25.3	24.4	36.4	22.1	35.7	27.4
Heat loss in water-cooling.	Nil	15.5	15.7	5.0	4.5	4.9	4.7	4.2

1. F. Clements.<sup>(1)</sup>2. C. L. Kinney and G. R. McDermott.<sup>(2)</sup>

3. Kinney and McDermott, results recalculated by W. Dyrssen.

4. W. M. Henry and T. J. McLoughlin.<sup>(3)</sup>5. Hypothetical figures of the Wärmetestelle, Düsseldorf.<sup>(4)</sup>6. R. D. Abbiss, *Iron Age*, 1934, vol. 133, May 24, p. 31.7. K. Rummel and G. Neumann.<sup>(5)</sup>8. A. Robinson, *Proceedings of the Lincolnshire Iron and Steel Institute*, 1929, vol. 2, p. 118.

The figures quoted in Table I. for Clements' balance (which refers to a single half-hour of the refining period) are different from those given in the original paper on account of recalculation on another basis. In Clements' original paper the heat absorbed in raising the temperature of the bath is set off against the heat of chemical reaction. The result is that the item "heat absorbed by steel and slag" does not appear in the final balance and the apparent thermal efficiency is zero. This illustrates the extreme importance, where comparisons are being made, of calculation along standard lines, and in Table I. the figures given by the various authors have been recalculated where necessary so that they are all on a comparable basis.

The high figure for the heat of chemical reaction in Clements' balance is due to this being restricted to the refining period when chemical heat plays a more important part.

Nevertheless, thermal efficiency is still a very useful guide to the effect of various conditions, and, defined in a special way, is made use of later in this paper.

Hampton<sup>12)</sup> has defined a "performance figure" for glass tanks (which are similar in many ways to open-hearth furnaces), but this expression is rather complicated and is really an expression of "no-load" heat consumption, which is a factor employed by many furnace technologists. The no-load heat consumption may be more simply determined by the use of the statistical methods outlined later.

For most purposes it is sufficient, and preferable, to consider the furnace simply as a melting unit, and to use as a basis the time required to melt the material charged. A fast-melting furnace is usually satisfactory in other respects. In the present paper the melting chamber is treated apart from the regenerators, as in this way it is easier to isolate the effect of differences in design of the upper part of the furnace.

### SECTION I.—METHOD OF CORRELATION.

#### *Standard Formula for the Melting Process.*

The time taken for a furnace to melt a solid charge is in theory given by :

$$t_m = \frac{H}{h - h_0} \quad \dots \dots \dots \quad (1)$$

where  $t_m$  is the time taken to melt the charge in hr.,

$H$  is the heat required to melt the charge in therms,

$h$  is the heat supplied to the melting chamber in therms per hr.,

and  $h_0$  represents the heat losses from the melting chamber in therms per hr.

This assumes instantaneous charging; in practice a definite time ( $t_c$  hr.) is required for charging the solid materials, and this will lengthen the time required for melting. Equation (1) then becomes :

$$t_m = \frac{H}{h - h_0} + k \cdot t_c \quad \dots \dots \dots \quad (2)$$

where it is assumed that for ordinary ranges of variation of  $t_c$ , other factors being equal, the relation between  $t_m$  and  $t_c$  is linear and of slope  $k$ .  $t_m$  is reckoned from the time of commencement of charging.

Equation (2) will be found most useful as a standard formula for the statistical examination of operating data, as it makes allowance quantitatively for several of the variables listed in the Introduction. For instance,  $(h - h_0)$  is the useful heat input to the melting chamber, and when calculated may be plotted against  $h$  to give the variation of thermal efficiency (defined here as  $(h - h_0)/h$ ) over a wide range of conditions by means of "characteristic curves."

The quantities  $t_c$ ,  $t_m$ ,  $H$  and  $h$  may all be found or calculated from the data available in the usual works records, provided that gas metering equipment is installed. The best quantities to use in the calculation of  $H$  and  $h$  are discussed in Section II. To calculate  $h_0$ ,

the unknown quantity determining efficiency, the only other knowledge required is that of the relationship between the melting time and charging time,  $k$ .

In theory, provided that charging is uniform, one would expect  $k$  to be equal to  $\frac{1}{2}$ , since if the first portion of the charge is put in at time 0, and the last at time  $t_c$ , the mean time at which the whole charge is in the furnace between times 0 and  $t_c$  is  $\frac{1}{2}t_c$  hr. Experimentally it is difficult to determine  $k$ . The value of  $k$  cannot be determined by plotting  $t_m$  against  $t_c$  for a large number of casts, and the only correct method is by partial correlation, taking  $H$  and  $h$  into account. The reasons for this are discussed in the Appendix, where it is also indicated that, unless charging conditions are very irregular, little error is involved by taking  $k = \frac{1}{2}$  as suggested by theory. Equation (2) therefore becomes :

$$t_m = \frac{H}{h - h_0} + \frac{1}{2}t_c \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

#### *Characteristic Curves.*

The use of statistical methods in connection with equation (3) greatly facilitates the use of the characteristic-curve method of

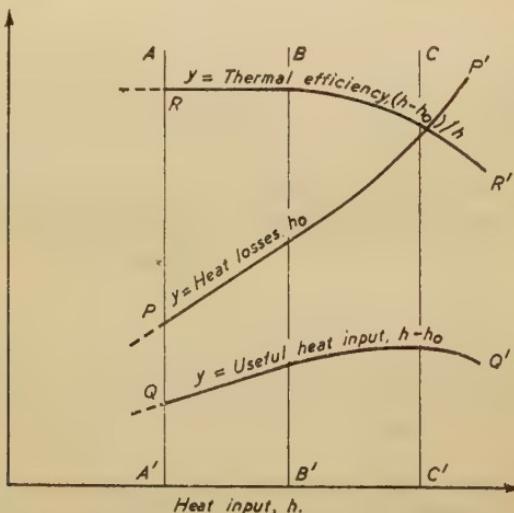


FIG. 1.—General Form of Characteristic Curves.

determining furnace efficiency. The original characteristic-curve method was principally developed by Armstrong,<sup>(13)</sup> Bentley,<sup>(14)</sup> Evans and Bailey<sup>(15)</sup> and Sarjant,<sup>(16)</sup> and by the Open-Hearth Committee<sup>(8)</sup> in constructing lines connecting fuel input and steel output. This relationship (analogous to the Parsons line in boiler investigations) is very well known, and is taken as linear over the ranges usually investigated. Extrapolation to zero output gives a

positive value of heat input - the no-load heat consumption of the furnace.

More useful information is given by making use of equation (3) to study the variation of useful heat input ( $h - h_0$ ), heat losses ( $h_0$ ) and thermal efficiency  $(h - h_0)/h$  with  $h$ . Fig. 1 is a diagrammatic representation of the types of curve obtained. The horizontal axis represents  $h$ , and the vertical axis the quantities  $h_0$ ,  $(h - h_0)$  or  $(h - h_0)/h$ ; the appropriate curves are  $PP'$ ,  $QQ'$  and  $RR'$ , respectively. Most furnaces operate within the range of  $h$  denoted by the vertical lines  $AA'$  and  $CC'$ . Between  $AA'$  and  $BB'$  the value of  $h_0$  rises with  $h$  according to a straight line the slope of which is less than  $45^\circ$ . The reason for this is that as  $h$  is increased by increasing the gas and air input the volume of waste gases, and therefore  $h_0$ , are correspondingly increased. Within this range  $(h - h_0)$  also increases linearly with  $h$ , although less steeply than  $h_0$ , and the thermal efficiency  $(h - h_0)/h$  is constant.

Between  $BB'$  and  $CC'$  the gas rate is approaching the maximum which the furnace can take. The curve  $PP'$  showing heat losses begins to rise more steeply, and the thermal efficiency  $RR'$  begins to fall. The effective heat input  $QQ'$  still rises, but eventually reaches a maximum at  $CC'$ . There are two possible reasons for these changes in the curves. The first slight alteration in slope may be due to heat being dissipated in fluxing of the brickwork by excessive heat supply. If, however, conditions are such that the line  $CC'$  is reached, this explanation is inadequate, and there is therefore strong evidence that the gas is not being properly burnt or that there is insufficient time for the flame to release its heat. In such a case the calculated value of  $h$  is incorrect.

Insufficient data are available to give information on the slopes of the curves at  $h$  values below  $AA'$ , as it is not practicable for open-hearth furnaces to run at low heat-input rates for any length of time. Under most conditions of operation it is preferable for a furnace to work at the  $h$  value represented by  $CC'$ ; whilst this will give maximum output but neither maximum thermal efficiency nor maximum economy in refractories, it is assumed that output is the first goal. If it is found that the furnace is working in the region to the right of  $CC'$  care should be taken to avoid an input of gas higher than that giving the  $h$  value represented by  $CC'$ .

Other interesting "characteristic curves" obtained by using equation (3) in various ways are those of thermal efficiency : Air/gas ratio, thermal efficiency through the week, and thermal efficiency through the campaign. Examples of these are given later.

In constructing curves of this type it is best to enter the appropriate details of  $t_m$ ,  $t_c$ ,  $H$  and  $h$ , air/gas ratio, &c., on separate cards for each cast. Fig. 2 is an example of a simple card of this kind, but more elaborate punched card systems such as the Copeland-Chatterson are easily adapted. For works with a well-equipped statistical department the extraction of the various relationships

should present no difficulty, particularly when sorting of the required data can be done mechanically. On the other hand, elaborate statistical equipment is not essential, and, provided that a simple adding machine is available, a complete correlation may be carried out in a few hours. To prepare a set of curves such as those of Fig. 1, data cards should be collected for 100 or more casts, and arranged in order of increasing  $h$ . These should be divided into groups of approximately equal numbers of cards, but not making divisions so that cards of the same  $h$  value appear in more than one group. For the successful determination of the curves there should be at least six groups with not less than fifteen cards in each group.

In each group the *average* value of the variables should be calculated, and, using these values in equation (3), a value of  $h - h_0$ ,  $h_0$  and  $(h - h_0)/h$  can be found for each group. These average values are used to construct the curves.

There are other ways of fitting curves to a large number of points, and for details of these reference should be made to standard textbooks on statistics. Such methods are, perhaps, slightly more accurate than the group-average method outlined above, but for a large

FIG. 2.—Example of a Card for Recording Operating Data.

number of points and for relationships which may not be linear so much arithmetical labour is involved as to make their use scarcely practicable.

Other correlations, such as the effect of the air/gas ratio and variations of efficiency through the week, may be carried out in a similar manner. In examining the effect of the air/gas ratio the data cards would be arranged in order of increasing ratio, whilst in studying variations through the week the groups would be taken as all the first casts, all the second casts, all the third casts and so on. Except in the latter case, it is advisable to eliminate all the first casts of a week from analysis, as these are generally abnormally long and their inclusion might have an adverse effect on the ease with which relationships can be traced. Similarly, any abnormal casts, such as those which have suffered from plant breakdowns, should be excluded.

#### *Examples of the Correlation of Data.*

Figs. 3, 4 and 5 are practical examples of characteristic curves, such as are outlined in Fig. 1, for a 40-ton, a 60-ton and an 80-ton

CAST No. ....	9.385
Cast of week .....	4 <sup>th</sup>
$t_c$ .....	3.25 hr.
$t_m$ .....	10.00 hr.
$H$ .....	1205 therms
$h$ .....	581 therms per hr.
Air/gas ratio .....	1.92

furnace, respectively. These show that the 40-ton furnace is working mainly in the  $AA'-BB'$  region of Fig. 1, although there is a slight fall in the thermal efficiency curve  $RR'$ , indicating that the region represented by  $BB'-CC'$  is being approached. With the 80-ton

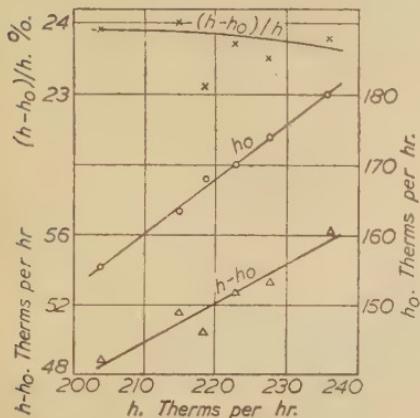


FIG. 3.—Characteristic Curves for a 40-Ton Furnace.

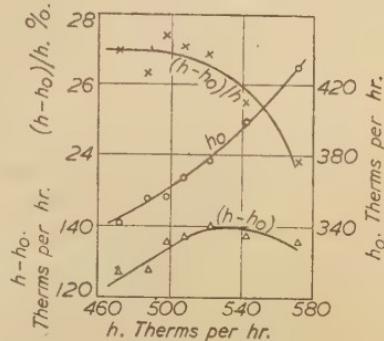


FIG. 4.—Characteristic Curves for a 60-Ton Furnace.

furnace this fall in the thermal efficiency curve is quite pronounced, showing that the furnace is being worked in the  $BB'-CC'$  region. The useful-heat curve  $QQ'$ , however, does not show any pronounced bend, therefore the optimum heat input for this design of melting chamber (which would be represented by the line  $CC'$  of Fig. 1) is not being approached closely.

The 60-ton furnace is the only one of the three in which the curve  $QQ'$  reaches its maximum. The slope of the  $h_0$  curve ( $PP'$ ) gradually changes from less than  $45^\circ$  to more than  $45^\circ$ , according to theory. It is clear that at times this furnace has been driven at an uneconomic gas rate, and that steps should be taken to restrict the ingoing gas flow to a value which will keep  $h$  below 530 therms per hr.

This optimum gas quantity is in this case 170,000 cu. ft. per hr.\*

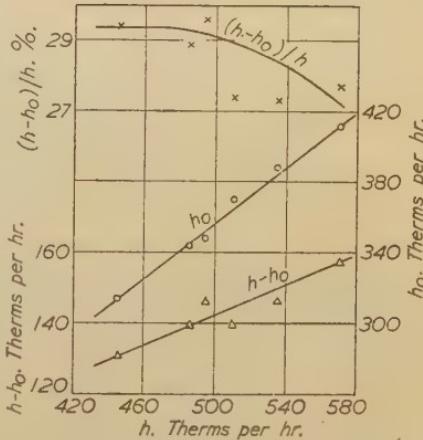


FIG. 5.—Characteristic Curves for an 80-Ton Furnace.

\* At a calorific value of 158 B.Th.U. per cu. ft., with 170,000 cu. ft. per hr. of gas preheated to  $1200^\circ$  C. and about 360,000 cu. ft. per hr. of air pre-

Since this furnace is attaining its optimum gas rate, whilst the others are not, it is probable that it is working at higher outputs and gas rates than the average. This is confirmed in Fig. 6.

If the ( $h - h_0$ ) curves ( $QQ'$ ) of all three furnaces are put on one diagram (as in Fig. 6), it will be seen that the 60-ton furnace has the highest  $h$  values relative to its size, and is taking correspondingly more gas than the others. It is of the Venturi pattern designed with

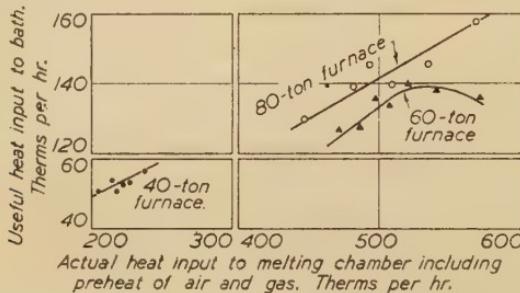


FIG. 6.—Thermal Efficiency of Open-Hearth Furnaces. Variation of *useful* heat input with *actual* heat input.

particularly generous passages, with the result that a large quantity of gas and air—even excessive quantities, as Fig. 4 shows—can reach the melting chamber.

When a furnace is not taking its optimum quantity of gas, as determined by the maximum of the curve  $QQ'$ , this is because either :

- (1) The passages are too small to permit this quantity of gas to enter the furnace with the gas pressure available, or
- (2) the design of the melting chamber is such that the supply of gas must be cut off before the optimum is reached to avoid damage to the furnace structure.

Which of these is the controlling factor is usually evident from working experience. If (1) is causing the limitation the furnace passages should be redesigned after pressure-balance calculations as outlined by the author.<sup>(27)</sup> If (2) is the limiting factor it is more difficult, in the present state of knowledge, to specify on a sound theoretical basis the alterations necessary. This also applies if the furnace is reaching its optimum heat input and it is desired to increase this. If, in experimenting with different designs of melting chamber and port, characteristic curves as outlined above are prepared from the results of each run, it can be seen at once whether there has been any real improvement.

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heated to 1300° C. (normal conditions for this furnace), the value of  $h$  is 530 therms per hr.

### *The Effect of the Air/Gas Ratio.*

Fig. 7 shows the effect of the air/gas ratio on thermal efficiency for two furnaces. In one case the optimum ratio has probably not been reached (the high efficiency at a ratio of 1·72 : 1 is not likely to indicate a real maximum). In the other, a definite maximum at 2·2 : 1 is apparent. However, some care must be taken not to interpret this too rigidly, as a low air/gas ratio, in furnaces where the air flow does not vary much, may simply mean that the gas rate is higher than usual. Under these conditions the theoretical

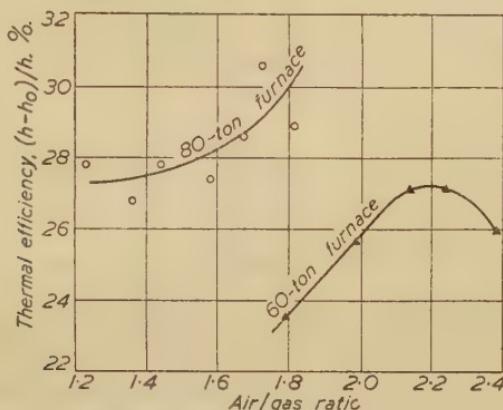


FIG. 7.—Variation of Efficiency with Air/Gas Ratio.

heat rate may be attaining the  $CC'$  value of Fig. 1, giving a low efficiency which would not necessarily be improved by increasing the air/gas ratio.

Both these furnaces were operating on producer gas, the theoretical air/gas ratio for which is about 1·3 : 1.

### *Variations through the Week.*

Figs. 8, 9, and 10 show the variation of melting time, rate of heat input and thermal efficiency through the week for three furnaces. (Since fewer results were available for the 60-ton furnace, the casts, except the first casts, are taken in groups of three.) Three outstanding facts are evident from these figures :

- (1) In two furnaces the shortest melting times occur in mid-week. The longer time required for the first cast is clear in all three.
- (2) In two of the furnaces the heat input  $h$  tends to fall as the week progresses.
- (3) The thermal efficiency is always lower early in the week, but there is little evidence of any other trend.

Whilst effects such as these have always been observed in an empirical way by practical operators, it is not easy to express the result quantitatively without statistical correlation as outlined above. Many of the variations observed are due to the obvious influence of the week-end shut-down, and Figs. 8 and 10 indicate that this influence persists well into the week.

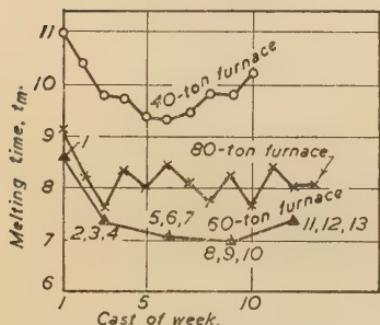


FIG. 8.—Variation of Melting Time,  $t_m$ , through a Week.

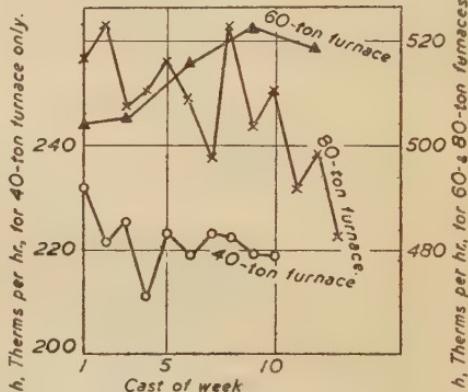


FIG. 9.—Variation of  $h$  through a Week.

The fall in  $h$  as the week progresses which is exhibited by two furnaces may be explained either by gradual tarring-up of the gas main and valves, causing a slight shortage of gas, or by a gradual increase in the "heat saturation" of the furnace structure, causing a reduction in the heat requirements of the furnace. Which of these

factors is operating may be revealed by a study of the variation of  $t_m$  as in Fig. 8. In the case of the 40-ton furnace the dip in the  $t_m$  curve in mid-week is very pronounced, whilst  $h$  gradually falls throughout the week. This suggests that at first the fall in  $h$  is due to decreasing heat requirements of the structure, as, although  $h$  falls, the melting time falls also. However, after mid-week  $t_m$  rises again; this is more what would be expected with falling values of  $h$ , so the slight fall in  $h$  during the second half of the week is probably due to the gradual tar-

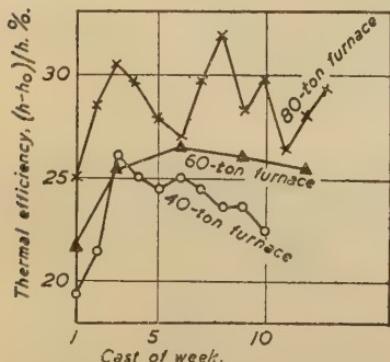


FIG. 10.—Variation of Thermal Efficiency through a Week.

ring-up of the gas main and valves.

The 60-ton furnace shows a similar trend of  $t_m$ , although  $h$  tends to rise. The rise in  $h$  rather suggests that there is no material increase

of main and valve deposits during the week, and that as the checkers and uptakes become thoroughly warmed up later in the week increased checker draught is available on the ingoing side to assist the incoming gas.

The 80-ton furnace shows a decrease in  $h$  with, after the first few casts, a fairly constant  $t_m$ . The fall in  $h$  is therefore due to more complete heat saturation of the furnace as the week proceeds.

Another explanation of the mid-week dip in  $t_m$  might be the human factor. When it becomes evident, say, about Thursday, that not more than a certain number of casts can be tapped by 1 P.M. on Saturday the men lose a certain amount of incentive to get casts out quickly. Incidentally, Figs. 8, 9 and 10 illustrate the great thermal advantages which would result from continuous practice, avoiding regular week-end shut-downs except where necessary for repairs.

#### *Variations through a Campaign.*

Fig. 11 shows the variations in thermal efficiency through a campaign, obtained by averaging the values for each variable for each week. This calls for little comment, as the trend is what might be expected.

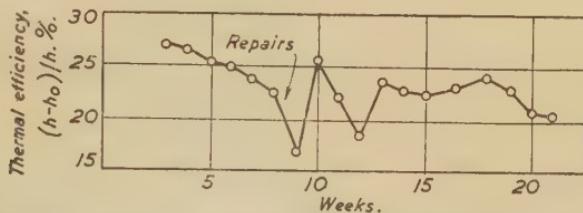


FIG. 11.—Variation of Thermal Efficiency throughout a Campaign of a 40-Ton Furnace.

The foregoing illustrations provide examples of the very useful quantitative information on furnace working which can be observed by making use of elementary correlation technique. Other simple relationships between important variables can be examined in a similar way.

#### SECTION II.—CALCULATION OF THE QUANTITIES INVOLVED.

Methods of calculating the various quantities employed in equation (3) are outlined below.  $t_c$  and  $t_m$  do not require calculation, being primary quantities which are recorded in every melting shop as a matter of routine. The thermal values  $H$  and  $h$  require calculation.

##### *The Calculation of H—the Heat Required to Melt the Charge.*

The heat required to melt the components of the charge depends on their composition. For instance, pig iron melts more easily

than scrap on account of its content of metalloids, and for similar reasons some kinds of pig iron and scrap melt more easily than others. There are three components of the charge to consider: Cold pig iron, scrap, and slag materials such as lime, ore and stone. Hot metal, being already molten when it reaches the furnace, is omitted from the calculation of  $H$ .

### *Pig Iron and Steel Scrap.*

Although the exact value of  $H$  depends on the composition, it is sufficiently accurate for the present purpose to take an average value applicable to either pig iron or steel scrap generally. Cast-iron scrap may be included as pig iron.

Values given in the literature (all in therms per ton) are given below; the figures in parenthesis are the melting points for which the  $H$  value is valid :

Authority.	Pig Iron.	Steel Scrap.
Richards <sup>(17)</sup> . . . . .	9.9 (1200° C.)	12.1 (1350° C.)
Clements <sup>(18)</sup> . . . . .	10.3 (1150° C.)	...
Wärmestelle, Düsseldorf <sup>(5)</sup> ( <i>loc. cit.</i> , p. 101) . . . . .	9.63–10.98	12.1–14.1
Spiers <sup>(19)</sup> . . . . .	9.14 (1100° C.)	11.8 (1500° C.)

The best averages for general use appear to be 10.0 therms per ton for pig iron and 12.1 therms per ton for scrap.

During the melting process pig iron loses carbon by oxidation and by diffusion into the scrap with consequent increase in melting point and  $H$  requirement. On the other hand the scrap gains carbon to a small extent, reducing the appropriate  $H$  value and so counter-balancing slightly the effect of the loss of carbon from the pig iron. It is difficult to allow for this in the calculation—the effect is quite small, and may be ignored.

### *Slag-Forming Materials.*

The slag-forming materials to be considered as part of the melting load are lime, limestone and such proportion of ore as is charged. It would be obviously incorrect to calculate the heat required for melting on the basis of the melting point of the pure materials. For instance, the lime, whether ore is added at an early stage or not, will very soon become contaminated with silica and iron oxide, and its melting point will be reduced by a considerable, although indeterminate, amount. The most reasonable way of calculating the heat required for melting the non-metallic materials charged would seem to be from the *weight* of the charged material and the *specific heat* and *melting point* of open-hearth slag. A higher  $H$  value is necessary for limestone on account of the heat required for calcination.

Values of  $H$  for slag-forming materials are given below, in therms per ton; the values for limestone are per ton of  $\text{CaCO}_3$  charged,

allowance having been made for the subsequent loss of weight in calcination :

Authority.	Lime and Oxide. Therms per ton.	Limestone. Therms per ton.
Richards <sup>(17)</sup> ( <i>loc. cit.</i> , pp. 29, 144)	14-21	26-30
Wärmetabelle <sup>(18)</sup> ( <i>loc. cit.</i> , pp. 100, 101)	18-20	27-28
Spiers <sup>(19)</sup> ( <i>loc. cit.</i> , pp. 127, 326)	14-5	25-3

As might be expected, there is considerable variation in these figures, on account of the uncertainty as to the melting point of slag (generally taken as from 1350° C. upwards). For general use 18 therms per ton for lime plus oxide, and 27 therms per ton for limestone are the *H* values suggested.

The most reasonable values suggested above are summarised below :

Material.	<i>H.</i> Therms per ton.
Cold pig iron and cast-iron scrap	10-0
Steel scrap	12-1
Lime and oxide	18-0
Limestone	27-0

### *The Calculation of h—the Heat Input to the Melting Chamber.*

The value of *h* is made up of the calorific value of the gas, the preheat of the gas and the preheat of the air. The measurement of prime importance is, of course, the measurement of the quantities of gas and air entering the furnace.

### *The Measurement of Gas Flow.*

Where reasonably clean gas such as coke-oven or mixed gas is used, measurement by the conventional orifice-plate methods presents little difficulty and need not be discussed further. Such a method is also fairly easy to apply to the ingoing air. On the other hand, hot raw producer gas, which is the most common fuel for open-hearth furnaces, is not easily measured. The difficulty is circumvented when a producer plant supplies one furnace only, as the gas rate can be computed from the coal consumption as given by the feed indicator or, better, as Sargent has shown,<sup>(20)</sup> from the rate of air supply to the producer, the air-flow/gasification-rate graph being linear. Producers linked to individual furnaces are not common, however, and the usual practice is for all producers to feed into a common main. Whilst this has obvious advantages from the point of view of plant operation, for metering purposes it renders necessary the installation of orifices or other measuring devices in the leads to each furnace. Methods which have been tried for the metering of producer gas have been :

- (a) The recording of the pressure drop across a Dyblie valve, or some bend in the flue.<sup>(21)</sup>
- (b) The measurement of the pressure drop across a damper.<sup>(22)</sup>
- (c) Pitot tube measurements.\*

\* Unpublished investigations of the Iron and Steel Industrial Research Council, and many experiments by individual works.

Measurements by Pitôt tube are not satisfactory for continuous recording, on account of the varying stratification taking place in most flues, which necessitates complete traverses at each reading. Measurement of pressure drop across bends, changes in section or reversing valves is only suitable for relative, not absolute, measurements, on account of uncertainty concerning the flow coefficient. Even if this is determined by calibration it is not likely to remain constant for long. For the recording of absolute flows, which is the only measurement useful for continuous control purposes, the orifice plate is the only satisfactory method.

The metering of raw producer gas was the subject of a special investigation of the Gas Producer Sub-Committee some years ago, and at the same time a commercial equipment was developed and placed on the market by a firm of instrument makers. This is an orifice method. The chief obstacles to the orifice method applied to hot raw producer gas are :

- (1) Deposits of tar soot, which reduce the orifice diameter, alter the contour, and so impair accuracy.
- (2) The week-end burn-out, where temperatures are very high, tends to spoil a metal orifice.

Difficulty (2) is got over by the use of a brick orifice, whilst (1) is avoided by the installation of steam jets which "blow" at intervals to remove deposits. According to Sinclair Kerr and others<sup>(23)</sup> it is possible to use an orifice made of steel in favourable locations where the crude producer gas is kept very hot, so that tar does not deposit (the plate being removed during burn-outs).

#### *The Measurement of Air Flow.*

The installation of an orifice for measuring air involves no technical difficulty, except that in many works space round the air intake is rather restricted. Open-hearth furnaces working on natural air depend on the "chimney effect" of the hot checkers and uptakes to induce the air required. This chimney effect is usually only very slightly more than the total resistance of the air passages, measured in inches of water-gauge. The installation of an orifice may cause sufficient additional pressure drop to prevent enough air from reaching the furnace ports, and it is usual to find positive air fans at furnaces where air is metered in this way.

If, after the installation of a meter, it is still possible to induce the air by the natural chimney effect of the regenerators the air meter will show less air than actually enters the furnace, on account of infiltration in the checkers and flues. The extent of infiltration may be measured by using a water-cooled Pitôt tube in the uptakes<sup>(24)</sup>; an example of actual figures obtained in this way is :

Air flow measured near valve	.	120,000 cu. ft. per hr. at N.T.P.
Air flow measured in uptakes	.	142,000     "      "

On the other hand, if a positive air fan is used, the air meter may read high, on account of leakage between the orifice and air port. Uptake measurements in positive-air furnaces have not yet been made, but unless the air fan is delivering at an excessive pressure it is not likely that such leakage will cause a serious error in the readings.

In the absence of more precise information it is suggested that with furnaces provided with positive air meters the meter be regarded as reading correctly the air entering the melting chamber, and that with furnaces provided with gas-metering equipment only the ingoing air volume be taken as 1·4-1·5 times the volume of producer gas, *i.e.*, approximately the theoretical plus 15%.

### *The Measurement of Gas and Air Temperatures.*

The difficulties involved in the measurement of gas \* temperature were comprehensively discussed at the Symposium on Gas Temperature Measurement held by the Institute of Fuel in December, 1938.<sup>(25)</sup>

It is well known that at gas temperatures above a few hundred degrees centigrade it is not possible to make temperature determinations simply by immersing a thermocouple in the gas stream. The gas temperature is seldom the same as that of the surrounding walls; consequently, the thermocouple reads a temperature intermediate between that of the gas and that of the walls, on account of interchange of radiation. Optical pyrometers tend still more to give the temperature of the surrounding walls.

The usual methods for obtaining true gas temperatures and which are discussed in the papers to the Symposium are (*a*) the use of several thermocouples of varying diameter, the readings being plotted against the wire diameter and extrapolated to zero diameter, which may be assumed to be unaffected by radiation to or from the thermocouple, and (*b*) the suction pyrometer in which an ejector or pump is used to draw the gases rapidly past the thermocouple tip (thus causing high convective heat transfer between gas and wire), steps being taken to shield the tip adequately from radiation from the walls. Recently Blackie<sup>(26)</sup> has proposed a very ingenious instrument in which thermocouples of varying diameter are connected partially in series and partially in opposition, so that all radiation errors are compensated for and the instrument reads the true gas temperature directly.

The above methods (with the possible exception of the Blackie pyrometer when this is commercially developed) are not suitable for continuous works recording. A method depending on the extrapolation of a set of readings to zero means excessive "office work" after the readings have been taken, whilst the suction pyrometer, with its connections for water-cooling and for suction and the necessity for frequent changes of the radiation shield, is too

\* The term "gas temperature" here refers to gas, air, or waste gas.

complicated to operate reliably and continuously. Nevertheless, the suction pyrometer is so far the most suitable method for measuring true gas temperatures, and notes on the construction and use of suitable instruments are given in the Symposium papers.

For routine control purposes reliance must be placed on the existing types of works instruments, and to investigate the corrections necessary special experiments with the more accurate, though troublesome, apparatus must be made. Experimental work with suction pyrometers<sup>(27)</sup> has shown that a fair estimate of the true temperature of the ingoing air may be obtained by *subtracting* about 200° C. from the mean temperature of the walls of the ingoing air uptakes, as measured by an optical pyrometer during the ingoing air period. A similar estimate of the waste-gas temperature may be obtained by *adding* 100° C. to the mean temperature of the uptake walls on the waste-gas period. In most furnaces the ingoing gas and air temperatures will be found to be between 1000° and 1200° C., and for the purpose of calculating the component of  $h$  due to preheat estimated values between these limits may be used.

From a knowledge of the gas temperature the heat content of the preheated gas and air can be obtained.

#### *The Heat Content of Gases.*

The specific heat of compound gases naturally depends on the composition, but a fair average for gases encountered in open-hearth practice is given in Tables II. to IV.; figures are given for intervals of 10° C., which is sufficiently accurate for all practical purposes. The figures are calculated from specific-heat data given by Spiers<sup>(19)</sup> (*loc. cit.*, p. 236) for dry gases.

These figures are also a near enough approximation for blast-furnace gas (although for more precise values 1% at lower temperatures and 2% at higher temperatures should be added).

#### *The Heat due to the Oxidation of Metal and Metalloids, and other Chemical Reactions.*

During the melting process the materials in the furnace are oxidised by the flame and by the furnace atmosphere. In addition, if a high percentage of pig iron is being worked, necessitating the charging of oxides, the ordinary steelmaking reactions (usually limited to the refining period) will take place to some extent. Consideration of this is, of course, very important in the hot-metal process.

The extent of flame oxidation during melting can be ascertained by comparing the mean analysis of the charge with that of the bath just after melting. From such data, N. H. Bacon \* has estimated that flame oxidation takes place at a rate equivalent to the addition of 13 cwt. of oxide per hour (in a 90-ton furnace). The amount of heat produced by the oxidation will depend on

\* Private communication.

TABLE II.—*Heat Content of Preheated Producer Gas (not including Calorific Value) Measured above 0° C.*

B.Th.U. per cu. ft. or therms per 100,000 cu. ft. Volumes measured at N.T.P.

Temp. °C.	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.
300	11.1	11.4	11.8	12.0	12.4	12.8	13.2	13.6	14.0	14.3
400	14.7	15.1	15.5	15.9	16.3	16.7	17.0	17.4	17.8	18.2
500	18.6	19.0	19.4	19.8	20.2	20.6	21.0	21.4	21.8	22.2
600	22.6	23.0	23.4	23.8	24.2	24.7	25.1	25.5	25.9	26.3
700	26.7	27.1	27.5	27.9	28.4	28.8	29.2	29.6	30.0	30.4
800	30.8	31.2	31.6	32.1	32.5	32.9	33.3	33.7	34.1	34.5
900	35.0	35.4	35.9	36.3	36.7	37.2	37.6	38.0	38.4	38.9
1000	39.3	39.7	40.2	40.6	41.0	41.5	41.9	42.4	42.8	43.3
1100	43.7	44.2	44.6	45.1	45.5	46.0	46.5	46.9	47.4	47.9
1200	48.3	48.8	49.2	49.7	50.2	50.7	51.1	51.6	52.1	52.5

TABLE III.—*Heat Content of Preheated Air Measured above 0° C.*

B.Th.U. per cu. ft. or therms per 100,000 cu. ft. Volumes measured at N.T.P.

Temp. °C.	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.
0	0.0	0.35	0.70	1.05	1.40	1.75	2.10	2.45	2.80	3.15
100	3.50	3.85	4.21	4.56	4.92	5.27	5.62	5.98	6.33	6.68
200	7.04	7.40	7.75	8.11	8.46	8.81	9.17	9.53	9.88	10.24
300	10.59	10.95	11.32	11.68	12.04	12.41	12.77	13.13	13.49	13.86
400	14.22	14.60	14.99	15.37	15.75	16.14	16.52	16.83	17.28	17.67
500	18.05	18.43	18.81	19.20	19.58	19.96	20.34	20.72	21.11	21.49
600	21.87	22.26	22.65	23.04	23.43	23.82	24.20	24.59	24.98	25.37
700	25.76	26.16	26.56	26.96	27.36	27.77	28.17	28.57	28.97	29.37
800	29.77	30.17	30.58	30.98	31.39	31.79	32.19	32.60	33.00	33.41
900	33.81	34.22	34.63	35.04	35.45	35.86	36.27	36.68	37.09	37.50
1000	37.91	38.32	38.74	39.15	39.56	39.98	40.39	40.80	41.21	41.63
1100	42.04	42.46	42.88	43.29	43.71	44.13	44.55	44.97	45.38	45.80
1200	46.22	46.64	47.06	47.47	47.89	48.31	48.73	49.15	49.56	49.98
1300	50.40	50.82	51.25	51.67	52.09	52.52	52.94	53.36	53.78	54.21

TABLE IV.—*Heat Content of Preheated Debenzolised Coke-Oven Gas (not including Calorific Value) Measured above 0° C.*

B.Th.U. per cu. ft. or therms per 100,000 cu. ft. Volumes measured at N.T.P.

Temp. °C.	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.
0	0	0.38	0.77	1.15	1.54	1.92	2.30	2.69	3.07	3.46
100	3.84	4.25	4.66	5.07	5.48	5.89	6.30	6.71	7.12	7.53
200	7.94	8.37	8.81	9.24	9.67	10.11	10.54	10.97	11.40	11.84
300	12.27	12.73	13.19	13.65	14.11	14.57	15.02	15.48	15.94	16.40
400	16.86	17.34	17.82	18.31	18.79	19.28	19.76	20.24	20.72	21.21
500	21.69	22.20	22.71	23.21	23.72	24.23	24.74	25.25	25.75	26.26
600	26.77	27.29	27.80	28.32	28.84	29.36	29.87	30.39	30.91	31.42
700	31.94	32.48	33.02	33.55	34.09	34.63	35.17	35.71	36.24	36.78
800	37.32	37.88	38.43	38.99	39.55	40.11	40.66	41.22	41.78	42.33
900	42.89	43.47	44.05	44.62	45.20	45.78	46.36	46.94	47.51	48.09
1000	48.67	49.27	49.87	50.46	51.06	51.66	52.26	52.86	53.45	54.05
1100	54.65	55.27	55.89	56.50	57.12	57.74	58.36	58.98	59.59	60.21
1200	60.83	61.45	62.08	62.70	63.32	63.95	64.57	65.20	65.82	66.45
1300	67.07	67.71	68.35	69.00	69.64	70.28	70.92	71.56	72.21	72.85

whether carbon, silicon, manganese, phosphorus or iron is being oxidised, but a fair average to take is 30 therms per hr. This is about 5% of the heat entering the melting chamber.

Bacon's figure was, however, obtained from keen furnaces working with an oxidising flame, and figures given to the author relevant to a 40-ton furnace working sluggishly owing to shortage of air and poor port design indicated flame oxidation varying from a negligible amount to that giving rise to an amount of heat equivalent to about 2% of the heat entering the melting chamber. Thus any allowance made for flame oxidation will depend on whether the furnace is working with a strongly oxidising flame or not.

In calculating the heat produced by flame oxidation of the charge it has been assumed that any carbon oxidised is oxidised to  $\text{CO}_2$ . It is reasonable to expect that the small volume of CO produced by carbon oxidation is at once oxidised to  $\text{CO}_2$  in an oxidising atmosphere. However, in the hot-metal process (or any process during the refining period), large volumes of CO are released from the bath following reaction between carbon and the oxides charged. The heat of chemical action should, therefore, as far as carbon oxidation is concerned, be reckoned only as far as CO; the CO gas evolved may be regarded as an additional gas supply to the furnace. In practice, the gas evolved from a "boiling" steel bath does contain some  $\text{CO}_2$ —according to Kalling and Rudberg,<sup>(28)</sup> about 2·5% of  $\text{CO}_2$ , 93·1% of CO (the remainder being small quantities of hydrogen and nitrogen). However, for the approximate methods of calculation now being considered, the oxidation of carbon in the molten steel bath may be considered as taking place as far as CO only.

This brings out one important point, which is often not appreciated in thermal calculations: That is that bath reactions, with the exception of  $\text{CO} \rightarrow \text{CO}_2$ , are 100% efficient, since they take place in the interior of the charge. On the other hand, carbon is oxidised only to CO in the bath; further oxidation to  $\text{CO}_2$  takes place in the furnace atmosphere, so that the thermal efficiency of the  $\text{CO} \rightarrow \text{CO}_2$  component of the heat of reaction will be no more than that of the fuel gas. In practice the efficiency will be even less than that of the fuel gas, as CO released from the bath near the outgoing end will tend to be swept unburnt into the waste-gas system. This is illustrated by the marked rise in checker temperature which often takes place during periods of vigorous reaction in the steel bath.

In steelmaking processes which use high proportions of hot metal, the period before the charge is completely melted may be divided into sections covering (1) the charging of the limestone, ore and scrap, and (2) the addition of the hot metal and completion of melting.

Period (1) is similar to the melting period of a cold-metal furnace; the chemical action is restricted to flame oxidation of the scrap, such slag-forming interaction as takes place between lime, silica and iron oxide, and the calcination of the limestone. The latter,

in the present calculation, is taken care of in the  $H$  value calculated for the heat required to melt limestone, and the net thermal effect of the other reactions may be considered to be up to 5% of the total heat entering the melting chamber in the fuel, as in a cold-metal furnace.

In period (2) the mass of hot metal causes reactions which take place on a much larger scale. Generally, after the addition of the hot metal there is a quiescent period during which the silicon is oxidised. The length of this period depends on the silicon content of the hot metal. Then follows a vigorous boil, during which the carbon is oxidised to CO. The bath gradually settles down, and becomes quiescent until melting is completed.

During the silicon oxidation, the net heat of the bath reactions is positive. However, the oxidation of carbon to CO does not liberate as much heat as the corresponding reduction of scale or ore absorbs, hence during the vigorous evolution of CO the bath tends to cool. Whether there is a net gain or loss of heat to the melting chamber as a whole depends on the extent to which the evolved CO can be burnt. Were it possible to complete the oxidation to  $\text{CO}_2$  in the melting chamber the net thermal result of the reactions would be a gain of heat to the melting chamber. In practice there cannot be anything like complete oxidation of CO in the melting chamber, and whether or not the net result of the bath reactions will be positive (as far as the melting chamber is concerned) will depend on :

- (1) The silicon content of the hot metal. High silicon will materially increase the amount of heat liberated in the bath. To a lesser extent this also applies to phosphorus.
- (2) The extent of CO oxidation in the melting chamber.

It is impossible to give any general rule applicable to the calculation of the net useful heat of chemical reactions in a hot-metal furnace after the addition of the hot metal. From calculations on a number of furnaces, it would not seem unreasonable to ignore this completely, assuming that a proportion of CO is oxidised and that silicon is present to a sufficient extent just to counterbalance the endothermic reactions. It may be assumed that flame oxidation will proceed to an extent giving up to 5% of additional heat, as has been assumed for cold-metal practice.

The above neglects the heat added to the melting chamber in the hot metal itself. However, only the cold charge is being considered, and, since the hot metal is not normally at a temperature sufficiently above its melting point to assist materially in the melting of the cold-charged materials, it also can be ignored in this calculation.

#### *Example of the Calculation of H and h.*

By the methods and from the data given above, these quantities may be estimated to a sufficient degree of accuracy for employment

in equation (3) as outlined in Section I. An example of the calculation is given below.

Consider a 90-ton cold charge, details of which are as follows :

*Composition.*

Scrap, 60 tons; pig iron, 30 tons; scale, 3 tons; lime, 5 tons; limestone,  $1\frac{1}{2}$  tons.

*Fuel.*

Gas flow, 210,000 cu. ft. per hr. (at N.T.P.), preheated to  $1050^{\circ}$  C.

Gas calorific value, 150 B.Th.U. per cu. ft. (at N.T.P.) net.

Air flow, 350,000 cu. ft. per hr. (at N.T.P.), preheated to  $1150^{\circ}$  C.

*Calculation of H.*

60 tons of scrap at $12\cdot1$ therms per ton . . . . .	726 therms.
30 tons of pig at $10\cdot0$ therms per ton . . . . .	300 "
8 tons of oxide plus lime at 18 therms per ton . . . . .	144 "
$1\frac{1}{2}$ tons of limestone at 27 therms per ton . . . . .	40.5 "
	<hr/>
TOTAL <i>H</i> . . . . .	1,210.5 ,,

*Calculation of h.*

Gas calorific value, 210,000 cu. ft. at 150 B.Th.U. per cu. ft. . . . .	315 therms per hr.
Gas preheat at $41\cdot5$ therms per 100,000 cu. ft. (Table II.) . . . . .	87.2 ..
Air preheat at $44\cdot13$ therms per 100,000 cu. ft. (Table III.) . . . . .	154.5 ..
	<hr/>
TOTAL <i>h</i> (fuel) . . . . .	556.7 ..
Add 5% for flame oxidation (assuming flame is keen and oxidising) . . . . .	27.8 ,,,
	<hr/>
TOTAL <i>h</i> (gross) . . . . .	584.5 ,,,

Assuming a 25% efficiency,  $(h - h_0)/h = 0.25$ , and a charging time of 4 hr., from equation (3) one would therefore expect a melting time of about  $10\frac{1}{4}$  hr.\* However, it must be strongly emphasised that equation (3) must not be expected to predict the melting time of individual casts, any more than a life insurance company can predict the life of an individual member of an occupation group from the accurately known life expectation of the group. Equation (3) can, however, be of great use in predicting the average change in melting time over a period which may follow a change in practice—say, the substitution of limestone for lime or a change in the average proportion of pig and scrap charged.

*APPENDIX.—The Variation of Melting Time with Charging Time.*

Several investigators have attempted to obtain the relationship between  $t_m$  and  $t_c$  by directly correlating values obtained in practice, with the object of obtaining  $k$  in equation (3) directly. This would only be possible if both  $t_m$  and  $t_c$  were completely independent of any

\* Alternatively, given the melting time, the efficiency may be calculated.

third variable, which is not usually the case. Generally, the rate of charging depends on the rate at which the earlier material is heated up, *i.e.*,  $t_c$  depends on  $h$ , just as  $t_m$  does. As  $t_c$  rises the  $h$  values tend to fall; this affects  $t_m$  as well, so that  $t_m$  rises by an amount considerably more than that due to the effect of the charging time alone. Therefore, the value of  $k$  obtained in this way will be much too high.

The correct way of determining  $k$  is by partial correlation as outlined in the text-books on statistics (*e.g.*, Udny Yule and Kendall.<sup>(29)</sup>) For the purpose of partial correlation the formula  $t_m = H/(h - h_0) + k \cdot t_c$  may be rewritten :

$$t_m = a + b_2 \left( \frac{1}{h} \right) + b_3 H + b_4 t_c, *$$

using Udny Yule and Kendall's notation, where  $b_4 = k$ . Then  $b_4$  is obtained from the simultaneous equations :

$$\Sigma [x_2(x_1 - b_2 x_2 - b_3 x_3 - b_4 x_4)] = 0 \quad . . . . . \quad (4)$$

$$\Sigma [x_3(x_1 - b_2 x_2 - b_3 x_3 - b_4 x_4)] = 0 \quad . . . . . \quad (5)$$

$$\Sigma [x_4(x_1 - b_2 x_2 - b_3 x_3 - b_4 x_4)] = 0 \quad . . . . . \quad (6)$$

where  $x_2 = \left( \frac{1}{h} \right) - \left( \frac{1}{\bar{h}} \right)$ ,  $x_3 = \bar{H} - H$ ,  $x_4 = \bar{t}_c - t_c$ . †

This gives the correlation between  $t_m$  and  $t_c$  when the changes in the remaining variables  $H$  and  $h$  are allowed for as far as this may be done with a linear equation.

Partial correlation involves a large amount of labour in arithmetical calculation, but  $k$  for four furnaces has been calculated in this way. Values obtained were 0.30, 0.44, 0.51 and 0.70. There is therefore another factor involved, and this is the non-uniformity of charging rate. If the rate of charging is increased towards the end of the charging period one would expect  $k$  to be greater than 0.5. For instance, taking extreme cases, if 90% of the charge could be crammed in during the last quarter of an hour of  $t_c$ , nearly all  $t_c$  would be non-effective and should be almost all subtracted, *i.e.*,  $k = 1$ . Conversely, if all the charge except one ton went in during the first  $\frac{1}{4}$  hr. and  $t_c$  was reckoned from the time when the last ton went in some hours later,  $t_c$  again would have little significance; this time  $k$  would be zero.

In most cases, unless it is known that the rate of charging is very uneven, no serious error will be introduced by taking  $k = 0.5$ . The absolute values of efficient and useful heat input may not be quite correct if the value of  $k$  is not exactly 0.5, but since the characteristic curves are chiefly useful for determining relative changes of the position of maxima, &c., the accuracy of absolute values is less important.

\*  $h_0$  does not appear, since, provided that one is working on the values which give a straight-line relation between  $h_0$  and  $h$  (this has to be checked by working it out beforehand, taking an arbitrary value of  $k$ ),  $h_0 = K \cdot h$ , and  $K$  disappears in the constant  $b_2$ .

† A "bar" over a symbol, *e.g.*,  $\bar{H}$ , implies the mean value of all the individual values. Clearly,  $\Sigma(\bar{H} - H) = 0$ .

The author wishes to express his thanks to the members of the Open-Hearth Committee and to the many steelworks managers who have freely placed operating data at his disposal.

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[This paper was discussed jointly with the preceding one by R. W. Evans on "The Heating of Open-Hearth Furnaces with Mixed Coke-Oven and Blast-Furnace Gas."]

*JOINT DISCUSSION.*

The papers by R. W. Evans on "The Heating of Open-Hearth Furnaces with Mixed Coke-Oven and Blast-Furnace Gas" and by A. H. Leckie on "The Study of the Thermal Performance of Open-Hearth Furnaces by the Correlation of Operating Data" were discussed jointly.

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Mr. A. ROBINSON (Appleby-Frodingham Steel Co., Ltd., Scunthorpe; Chairman of the Open-Hearth Committee): The paper by Mr. Evans shows the difficulties in using mixed coke-oven and blast-furnace gas, gives suggested reasons for these, and makes certain practical suggestions for coping with these difficulties. That these difficulties are real is well known to furnace operators who have changed from producer to mixed gas.

I agree with the author up to a point when he says that good mixing of air and gas is necessary, but we do not require too great a turbulence, or the roof suffers, nor too short a flame, or the bath boils at one end of the furnace only and not over its full length. Combustion must be completed in the hearth, but a blanket of flame over at least three-quarters of the furnace bath is required, as is in fact admitted by the author. There can be no disagreement with the author on the much greater effect of radiation as compared with convection, although this is not so noticeable until the charge is flat in the furnace.

There is a noticeably greater tendency for the slag to foam when working with mixed blast-furnace and coke-oven gases, in spite of all that may be done to see that the gas checkers are hot enough to crack the gases. The author makes certain suggestions as to the cause. Moisture in the gases has been suggested in other quarters, and the rapid building up of a reserve of heat in the charge to carry it quickly over a certain critical range of temperature seems to be fairly generally accepted. I think that the composition of the slag has something to do with the tendency to foam, because certain charges are certainly more inclined to foam than others.

The addition of tar or pitch or similar materials to the gas has an almost magical effect on the foam, by apparently increasing the flame luminosity and therefore its radiating power. What is the difference between this luminosity and an apparently similar one obtained by cracking the gas? The author has attempted to explain this. Has he noticed an envelope on the cracked-gas flame which is non-luminous and has the appearance of burning hydrogen?

The loss of calorific power when cracking the gas may be the reason why it is necessary to use a mixed blast-furnace and coke-oven gas of higher calorific power than the producer gas which it replaces—about 230 B.Th.U. as against 175 B.Th.U.

The suggested method of introducing the coke-oven gas with tar and only regenerating the blast-furnace gas has a sound basis, but it depends upon tar supplies and the economics of its use.

The difficulty in an open-hearth furnace that the gas entry and exit ports must be of the same size is certainly increased when using mixed gas, and the emphasis laid upon greater care in building the furnace and keeping the furnace structure air-tight as much as possible is well founded. I agree also with the greater need for adequate instrumentation. The intelligent use of the damper is necessary at all times, and a foolproof 100% automatic damper control working with the very small pressure in the furnace is required.

From our experience, I cannot agree that the dolomite consumption with mixed gas is lower than with producer gas. Our experience is slightly the other way, and the gas is certainly more severe on the brickwork.

I must congratulate the author on a painstaking explanation of the difficulties of using mixed gas and the methods of overcoming them, but I must point out that mixed gas is being used successfully without any tar additions.

Dr. Leckie's paper is of a type which is rare, namely, a link between the scientific and the practical types. Much thought and observation on the actual furnace have gone into its production, and the paper is one to be recommended to the open-hearth manager, as it gives him a simple and easy way of evaluating his furnace efficiency from a thermal standpoint, and the effect of any alterations he may make in his furnaces—the effect of adequate or dirty checkers, variation in port design, stack draught and so on.

On the second page of the paper, when dealing with variables affecting open-hearth furnace performance, in (b) I should prefer to see the words "up to a limit" instead of "in general," as each furnace has its optimum requirements (a point which the author makes later on), there being a limit to the speed of transfer of heat. The attempt to go beyond this point does no good; it wastes fuel and often brings disaster to the furnace.

The author confines himself to considering the furnace as a device for transferring heat, and, at that, to the hearth only. It may be that some modification of the general form of the characteristic curves and/or the lines A, B and C (Fig. 1) will be necessary if the whole furnace is considered. Similar curves including checkers would be very interesting.

In considering Fig. 1, the curve QQ' is a general measure of the furnace output when working. I suggest that the best operation of the furnace is much nearer BB' than CC', for, though while the furnace is working some small advantage may be gained in output, the heat loss rises rather steeply, and a greater and greater portion of this is used in destroying the furnace structure. On balance, therefore, taking account of the more frequent repairs

which would be necessary at  $CC'$ , the yearly output would not be as great as nearer  $BB'$ , and the cost of the steel made, due to those more frequent repairs and the greater fuel consumption, would be greater. Whilst output may be the first goal (though this is a matter of argument), it is average output, including the time lost through repairs, which counts. The curve  $QQ'$  is almost horizontal on reaching  $CC'$ , and for some time before this, extra gas seems to be employed for no useful purpose—that is to say, it is wasted. Many furnaces are using too much stack draught and getting too much gas through them, and the correct use of the damper will improve the thermal efficiency and the output of the furnace.

Taking the figures as a whole, these curves should be very useful to show up deficiencies in design and allow a check on alterations. An examination of the furnace on these lines will give a starting point from which variations in design can be made to try out suspected shortcomings.

The author touches on the effect of the week-end stoppage and the human factor. It is very noticeable that a furnace which starts the week well finishes with a good output, but a bad start is seldom recovered.

At the end of the paper the author has omitted two materials in the calculation of  $H$  which perhaps he does not consider as useful employment of heat, namely, the burnt dolomite used for fettling and the loss by wear on the furnace structure, both of which go into the slag and both of which, unfortunately, are part of the working of the process. Moreover, a figure giving the heat requirements of hot metal to steel would round it off.

In the Appendix the author gives four values of  $k$ , from 0.30 to 0.70. Personally, I should expect it to be more than 0.5 with even charging, owing to the constant opening of the doors. The author asserts that the variation from 0.5 is of no great importance in the circumstances, but it would be of interest if he could give particulars of the methods and times of charging and the quantities in each case shown.

Mr. J. N. KILBY (Hon. Member of Council; Messrs. Richard Thomas & Co., Ltd., Scunthorpe): The fact that Mr. Evans' paper takes into account the experience of a 100% change-over from producer gas to mixed gas adds to the importance of the views expressed and conclusions arrived at. The author states, and truly, "It is evident . . . that a melter who has spent his life on producer-gas furnaces has considerably to increase the scope of his knowledge when introduced to mixed gas." The newer physical, chemical and thermal effects of flame and heat development demand more from the melter, and his response will be reflected in the results obtained, *i.e.*, ingot output per hour and sales yield in the mill.

In his conclusions the author refers to the scrapping of producer plant when coke-oven gas and blast-furnace gas become increasingly

available, and states that the most searching deliberation should be given to the most efficient utilisation of the total gas surplus, with which I agree.

The author recommends as the best method of firing open-hearth furnaces the use of cold coke-oven gas and tar, tar oil or pitch. The Redbourn plant adopted this policy some years ago, and, with the exception of a minor section producer-gas-fired to act as a buffer taking care of fluctuations in general conditions, the furnaces are fired with cold coke-oven gas and tar or pitch, and very good results have been and are being obtained. However, with the price of coal what it is, the firing of open-hearth furnaces may call for further review.

The author says in the last paragraph "An open-hearth operator who has confidence in the regularity of his heat input and resulting flame temperature is relieved of at least half his normal troubles." This is true. I have the impression that the author does not feel this to be the case with mixed gas, and if I am correct in this surmise this becomes the major point in his paper. In my opinion, blast-furnace gas should not be used in the steel shop. Whilst it may be tempting to apply this "surplus" heat accompanied by a low initial expenditure in the open-hearth plant, other and more suitable and efficient uses should be adopted.

As regards foaming slags, during recent years much attention has been drawn to this subject, and it has aroused healthy discussions. I believe this increased attention is due to greatly increasing occurrences of foaming and not to keener observations. Whilst I agree with the author that the quality of the flame has some effect upon foaming in many cases, there are other and equally important causes. We have experienced foaming slags throughout the history of basic open-hearth production, and in cold-stock producer-gas-fired furnaces my experience has been that the trouble was chiefly due to iron quality, with a definite relationship to the silicon and total-carbon contents, and occasionally to badly worked charges.

Operating on hot metal, and firing with either cold coke-oven or producer gas, our experience indicated that foaming slags were primarily related to the raw materials and quality of the slag. Methods and sequence of charging also had some influence.

I appreciate the present-day difficulties of the blast-furnace operator; nevertheless, there is more than a strong relationship between the quality of the pig iron and the efficiency of all the open-hearth operations and the evil of foaming slags. From observations and detailed records over a period of seven years at the Redbourn works, with an elasticity of 45–80% of hot metal, the steel output per hour, the life of the steel furnaces, the fulfilment of the programme and the ultimate sales yields definitely proved this tie-up.

Dr. DAVID BINNIE (The Lancashire Steel Corporation, Ltd.,

Irlam, near Manchester) : In Fig. 5, Dr. Leckie has drawn the characteristic curves for an 80-ton furnace which shows a pronounced fall in the thermal efficiency curve  $RR'$ ; also the useful heat curve  $QQ'$  goes up almost as a straight line. Dr. Leckie remarked that since the useful heat curve  $QQ'$  does not show any pronounced bend, therefore the optimum heat input for this design of melting chamber is not being approached closely.

The curve  $QQ'$  can be deduced from the curve  $RR'$  by multiplying the points on  $RR'$  by the corresponding abscissa readings, which gives a curve convex upwards with a flattening at the maximum at the right-hand side, indicating that the optimum heat input for this design of melting chamber was being approached. On the other hand, if the curve  $RR'$  is deduced from the curve  $QQ'$  the curve  $RR'$  becomes of the concave-upwards type, confirming that the curve  $QQ'$  in Fig. 5 should have been drawn more in accordance with the shape of the  $QQ'$  curve in Fig. 1 between the limits  $AA'-CC'$  than with the straight or nearly straight line shown.

How was the air/gas ratio determined for the furnaces shown in Fig. 7 ? Was it measured at the fan or in the up-takes, or was it determined by waste-gas analysis ?

The air/gas ratio of 2·2 : 1 implies almost 70% of excess air above that required for combustion. Would not the use of such a large amount of excess air be expected to lower the furnace efficiency by virtue of the amount of sensible heat carried away by the waste gases ?

Mr. R. A. HACKING (Messrs. Dorman, Long & Co. Ltd., Middlesbrough) : I should like to support Mr. Evans' statement on the last page of his paper that the best method of firing open-hearth furnaces is to use cold coke-oven gas and tar-oil or pitch. This implies that in a composite plant coke-oven gas should be reserved for open-hearth furnace use, whilst the blast-furnace gas would be devoted to other purposes, such as steam-raising, ingot, billet, bloom and slab reheating, &c. Blast-furnace gas can be applied just as efficiently as coke-oven or mixed gas to the firing of boilers and in ingot-soaking furnaces. I consider that blast-furnace gas alone is even superior. In the case of reheating furnaces for blooms, billets, slabs, &c., there is not much to choose between them, but our experience is that it is generally desirable to use a proportion of coke-oven gas in admixture with blast-furnace gas for that purpose.

In the open-hearth furnace, control of the direction and character of the flame is probably the most important single factor determining thermal efficiency, refractories consumption and output. In this regard, the use of cold coke-oven gas removes the very serious disability of producer-gas-fired or mixed-gas-fired furnaces in which the block design must of necessity be a compromise between what is good at the ingoing end on the one hand, and the outgoing end

on the other. When the air only is regenerated, this consideration disappears, and in several well-established designs excellent flame direction can be maintained throughout the whole length of a campaign. The same considerations also facilitate substantial prolongation of the time between rebuilds, and with the Hoesch design of furnace we have had campaigns of over a year.

Latterly we have been getting away from the Hoesch design in an endeavour to avoid the heavy loss of thermal units in the cooling water, which, in that build, is round about 20%. During the last 18 months or so, we have developed the use of a block something like that used at Port Kembla, as described by Knight.<sup>1</sup> In two 100-ton furnaces, this build has reduced the cooling-water heat loss to considerably less than half the Hoesch figure, control of flame direction has been maintained and even improved, whilst substantial economies have been achieved in refractories consumption. Another advantage of the new design is that it gives greater flexibility in regard to the proportion of tar used to give luminosity to the flame. This, incidentally, was one of the main reasons which led to its development and installation at our plant. Recovery after stoppages incurred by air raids, &c., in the case of the older design of cold-coke-oven-gas-fired furnace was slow and the effect upon output serious. The greater flexibility of the Port Kembla block in regard to the thermal input from coke-oven gas and tar, respectively, has largely removed this disability, with the result that the two units mentioned above now lead the shop in recovery after involuntary stoppages.

It would be interesting to add to Fig. 8 of Dr. Leckie's paper corresponding curves for cold-coke-oven-gas-fired furnaces, and to this end I will endeavour to supply the necessary statistics for typical units.

**Dr. T. P. COLCLOUGH** (Ministry of Supply, Iron and Steel Control, London): The paper by Mr. Evans is particularly opportune, because one of the fundamental problems is to decide the type of open-hearth furnace to be adopted after the war. The evidence submitted in this paper supports the experience in other works, that mixed gas alone is not an ideal fuel for open-hearth furnaces. The necessity for cracking mixed gas and the conditions under which this operation must be carried out make it extremely difficult to design a furnace suitable for cracking gas and at the same time to ensure good combustion.

Experience has proved the value of cold coke-oven gas, but it is necessary to emphasise the necessity of adding some illuminating agent. Attention should be drawn to the excellent results obtained in America by the use of low-grade fuel-oil residues. Furnaces using fuel-oil residues alone, without coke-oven gas, show

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1943, No. I., p. 233 P.

heat consumptions of about 3 million B.Th.U. per ton of ingot as compared with the old bogey of 4 million B.Th.U. with mixed gas. A combination of coke-oven gas with fuel-oil residue or tar has definite advantages over mixed gas for steelmaking.

A further point of importance is that the adoption of this principle would result in a considerably reduced cost of construction of the open-hearth furnaces and plant by the simplification of the regenerator system, valves and flues, and the elimination of gas producers.

**Mr. J. H. WHITELEY** (Consett Iron Co., Ltd., Consett, Co. Durham) : I would like to ask Mr. Evans one or two questions in connection with the subject of his interesting paper, for I have had no experience in the use of mixed gases in open-hearth furnaces. It is stated that the calorific value of the gases used was between 200 and 230 B.Th.U. and that for some obscure reason the basic slags then tended to foam badly in the refining stage. Is that trouble still as pronounced when the calorific value is lowered to say 170 B.Th.U., a figure nearer that of producer gas? I would also ask Mr. Evans whether the use of mixed gases in the acid furnace affects the quality of the steel in any way. As is well known, a committee was formed a few years ago to study hair-line cracks, and the evidence so far obtained strongly indicates that hydrogen plays a large part in their formation. It is generally conceded that acid steel made in producer-gas-fired furnaces is much less prone to that defect than either basic open-hearth or electric steel, and it may be that the use of mixed gases with their comparatively high hydrogen content might make acid steel more liable to have hair-line cracks.

There is only one point in the paper on which I have any comment to make. Mr. Evans states that with mixed gases the conditions in the furnace are much less oxidising than with producer gas, and he attributes that to the reducing action on the slag of hydrogen liberated in the body of the furnace by the decomposition of water vapour in the gases. That explanation seems to me to be a very dubious one, for hydrogen, being a light gas, would tend to rise rather than fall and pass away down the ports, especially if the air port is overhead. The oxygen which is also liberated would, I think, be more likely to impinge on the slag.

#### JOINT CORRESPONDENCE.

**Mr. M. W. THRING** (The British Coal Utilisation Research Association, London) wrote : The clear evidence that Mr. Evans gives that a foaming slag is due to insufficient luminosity in the heating flame provides a further link in the chain of evidence which indicates that in the open-hearth furnace as at present designed

there is very little preferential heat transfer to the charge as compared with the crown. There are two ways by which it would be possible to arrange that the charge in the furnace would receive more heat than the crown, even when they are at the same temperature, but the following argument would appear to indicate that the only reason why the charge receives more heat than the crown is that it is at a lower temperature.

These two possible ways are :

(1) The use of a relatively opaque flame, so arranged as to be hotter at its inside than at its top, and hence to blanket the radiation of the hottest part from the crown. The use of a stagnant layer of cold air over the flame would not have any effect, since this is perfectly transparent. Using a heat-flow meter, Baulk<sup>1</sup> has shown experimentally that, at any rate in a glass furnace, the flame tends to be cooler underneath when there is cold material underneath it, and hence that this condition is not satisfied in actual furnaces.

(2) The second possibility is that the flame is made to give up appreciably more heat to the charge than the crown by forced convection on the former, resulting from the downward direction of the ports, while the latter is protected by a stagnant layer.

If the second explanation were correct, a flame which is non-luminous would give a considerably greater preferential heat to the charge, as compared with the crown, than a luminous flame, since it would give up relatively more of its heat by convection. Now, the evidence that a non-luminous flame causes a foaming slag indicates that such a flame tends to give up, if anything, a greater fraction of its heat to the crown than does a luminous flame. This would appear to indicate that there is practically no preferential heating due to forced convection. If this is so, it follows that the only reason that the steel receives more heat than the crown in the furnace is its lower temperature. Further evidence for this is given by the fact that the back part of the crown over a Naismith sloping back wall usually becomes rather hot, presumably because it is not over cold steel but over hot refractory.

This matter is clearly of the highest importance, since the furnace design in which preferential heating of the steel as opposed to the crown was obtained would clearly reduce the load on the silica crown enormously. This indicates the value of the information which will be obtained if it is found possible to utilise the heat-flow meter now being developed by the British Coal Utilisation Research Association for measuring separately the convection and radiation in an open-hearth furnace. The instrument has hitherto been used only in a glass furnace.

<sup>1</sup> To be published shortly in *Coal Research*.

Mr. T. F. PEARSON (Messrs. Colvilles, Ltd., Cambuslang) wrote : The subject matter of Mr. Evans' paper is of extreme interest and importance, and similar ground has been covered in a paper<sup>1</sup> by my colleague, Mr. Wright, and myself. There are a number of points of view in both that are common, but in the light of my own subsequent experience original views held have undergone some modification and Mr. Evans raises certain points which are controversial.

Undoubtedly the application of clean gases to melting furnaces has stimulated interest in the properties and characteristics of flame, since operational difficulties have been encountered when comparison is made with the older standard of producer-gas firing. Increased interest has centred itself on the problems of rate of heat transfer and the greater incidence of foaming in basic charges. With regard to flame characteristics, in the absence of absolute experimental data much must be conjectural. I consider, however, that the position with regard to foaming is becoming more well-defined. Foaming *may* be due to a high surface tension in the slag, but since some charges foam and others do not, even under mixed gases, and since such slags may cover a wide range in composition, I still suggest that all basic slags possess the ability to foam, and that the fundamental reason for foaming is lack of heat, and not some single physical or chemical property of the slag. Professor Hay<sup>2</sup> has shown that certain slags (including actual furnace slags) can foam if agitated by a gas; over a range of temperature and above and below this range a true liquid exists. In the course of some work on a large tilting furnace fired by mixed gases I have found instances of a "stepped temperature" gradient in charges which foamed, due to the sum total of the reactions taking place at that time being apparently endothermic and the heat transfer from the flame being insufficient to prevent this fall in temperature. This would appear to me to be the reason why increasing proportions of hot metal increase the likelihood of foaming, since the risk of arriving at an endothermic period becomes greater, owing to the greater amount of buried oxide necessary to control the value of the melt.

It appears to me, therefore, that the theory of lack of heat, together with the possibility of a stepped temperature gradient within the bath, is more consistent with practice than any postulation with regard to any one physical or chemical property of the slag. As an example, even finishing slags, which are not so highly siliceous as early slags, and of which the surface tension, viscosity, &c., may be lower, can be made to foam easily if their temperature is not high by causing a still further depression of temperature (probably into some such range as indicated by Professor Hay)

<sup>1</sup> W. B. Wright and T. F. Pearson, *Journal of the West of Scotland Iron and Steel Institute*, 1941–42, vol. 49, Part II., p. 23.

<sup>2</sup> Private communication.

by feeding oxide or scale. Such a foaming phase is, however, usually transient only, because the recovery of temperature is much more rapid. Such a theory fits in with the effect experienced in taking gas off a bath which is foaming, when the foam tends to rise. I discount the pressure effect suggested by Mr. Evans, and also suggest that the disappearance of foam when the bath carbon content reaches 0·2–0·3% may be due not to retarded bubble formation but to the general increase in temperature arrived at by this time.

From this point, however, the view is held in common with Mr. Evans that the character of the flame is all-important, and I suggest that the essential necessity is to convert the flame into a "body" more closely approximating to a "black-body" radiator, so that the quantity of heat transfer per unit time and area becomes greater and so prevents or narrows down the foaming range to insignificance, resulting in a smoothly ascending temperature gradient.

Flames generally, even apparently luminous flames, have comparatively low emissivities, and there are enormous gaps in their radiant-energy curves over all wave-lengths when compared with the continuous smooth energy curve obtainable from a true black body. As mentioned in my paper, carbon dioxide and water vapour radiate only on three narrow energy bands within the measurable range (0·4–21·0  $\mu$ , approx.). All these radiations travel with the speed of light, and so contradict Mr. Evans' statement on p. 397 P that "the great evolution of heat within the flame cannot be dissipated quickly enough."

The injection of an illuminant into a mixed-gas flame therefore fills up some of the gaps in the radiated-energy curve by reason of the presence of solid particles which are capable of radiating on all wave-lengths. Hence, the emissivity and consequently the transfer of heat increases. It has been suggested to the writer by Dr. McCance that the absorption spectra of foaming slags themselves may present interesting features, in that, under certain gaseous flames, peaks in the flame spectrum may coincide with gaps in the slag spectrum, hence precluding any possibility of heat transfer over such a wave-band.

Such a theory still emphasises the desirability of developing a flame more nearly a black-body emitter, so that the whole energy wave-band is adequately covered, so ensuring the maximum transfer of heat. May this not fit in better than Mr. Evans' postulation regarding "actual" and "apparent" luminosity on p. 402 P?

I suggest that compressed blast-furnace gas is preferable to compressed air for the injection of liquid fuels, since it must be remembered that primary aeration of any fuel tends to lower the luminosity attainable (p. 408 P). Mr. Evans' instrument specification is elaborate, but I would be grateful to learn if he has found a satisfactory tar flow indicator. I am not quite in sympathy with

the "indispensability" of temperature indicators in the blast-furnace and coke-oven mains entering the shop, because, whilst I realise that the humidity of the gases is of importance, if I encounter recorded values which are very high and therefore objectionable I am still left with no alternative procedure by which to compensate for them.

Mr. Evans' remarks under "Metallurgical Considerations" are interesting. I have not, however, observed any noticeable change in the loss of manganese added to the bath—attributable to the use of mixed gases. This lower loss will tend to occur if the "oxide" in the slag is lower certainly, but may not the lower "oxide" in the slag be a result again of difficulty in securing high bath temperatures early in the finishing stage and not entirely to the chemical characteristics of the flame—thus being illustrative of the point that Mr. Evans makes regarding the "lesser flexibility" of mixed-gas-fired furnaces?

Mr. S. W. EVANS (Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd., Cardiff) wrote : The necessity of a highly luminous flame in open-hearth steelmaking is now generally recognised by all operators of mixed gases. Mr. Evans has rightly stressed the importance of this during periods when the heat input has to be transferred through slag. Owing to the non-conducting nature of the latter, sufficient heat cannot be absorbed from the flame by means of conduction, convection and gas radiation (from polyatomic molecules of steam and carbon dioxide) in order to melt the charge without damage to the furnace structure. Hot radiating carbon skeletons must be produced by breakdown of hydrocarbons, by means of a high temperature of regeneration.

As the author has shown, there is evidence of loss of calorific value when coke-oven gas is preheated, but is it not possible for the increased rate of heat transfer which results from the luminous flame to more than counterbalance the drop in flame temperature? With regard to the suggested method of firing, *viz.*, by means of regenerated blast-furnace gas, cold coke-oven gas and tar, I consider that this would be inferior to mixed-gas regeneration. Tar cannot give the same efficient luminosity as high preheats; the flame is inclined to be black and appears to be of lower temperature, whilst preheated mixed gas gives a streak of silver. Loss of direction also appears to accompany the use of tar injected by steam. If possible, the best position for introducing the tar would be at the entrance to the gas regenerator, when intimate admixture with the gas and cracking, similar to that which takes place with producer gas, would occur.

Whilst the limitation of mixed gas operations according to the methane content of the coke-oven gas is generally acceptable, the author's tabulation on p. 410 P gives rather conservative values. At these works, stationary furnaces of 85–90 tons tapping capacity

have worked, in 1937-38, under practically the same conditions. Briefly these are :

Heavy hydrocarbons	in coke-oven	:	:	2·0%
Methane	gas	:	:	24-26%
Hydrogen		:	:	59-62%
Temp. of coke-oven and blast-furnace gases				18-25° C.
Gas and air checker top temp.				1050-1200° C.

Frequency curves are plotted in Fig. A on a charge-to-tap basis, for three groups of charges :

	Hot Metal.	Silicon.	Phosphorus.	Manganese.
I.	40-45%	0·2-0·4%	1·4-1·6%	1·5-2·0%
II.	52-57%	0·2-0·4%	1·2-1·4%	1·5-2·0%
III.	67-72%	0·2-0·4%	1·5-1·7%	1·5-2·0%

These curves show that increasing the hot metal up to approximately 55% does not result in delayed heats, but when 70% is reached the proportion of charges taking 11-12 hr. is practically equal to the number taking 9-10 hr. from charge to tap. Foaming during the melting period has lengthened the time.

The limit for satisfactory working with 24-26% of methane in the coke-oven gas is therefore in the region of 55-60% of hot metal. For these charges as much as 5-6 tons of Swedish or Brazilian ore would have to be included in the charge.

In considering the curves in Fig. A it may be pointed out that the charging conditions were fairly constant, *viz.*, three machines available for four furnaces. In working the high-metal charges no definite slag-off policy was adopted; if any ran off when the charge swelled up during the melt, it was allowed to do so, but could not be stimulated.

Under mixed-gas operations when gas-holders are in use, the heat input can be controlled to fine limits. The flame is very hot and the scrap is rapidly "cut down." Some loss of luminosity is liable to occur, unless

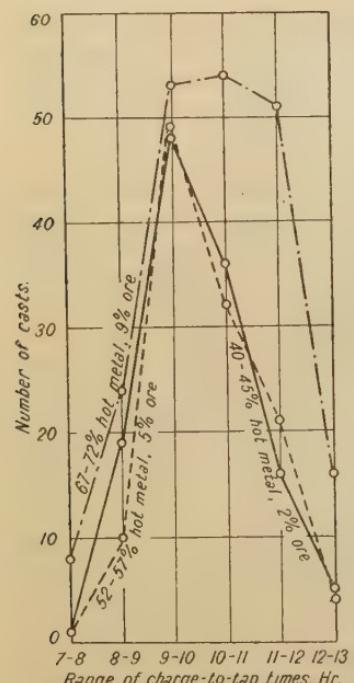


FIG. A.—Frequency Curves of Charge-to-Tap Times for three groups of charges.

the maximum possible volume of gas is carried in order to prevent the checkers from "going back." Scrap must therefore be charged rapidly. The optimum time for the 52-57% hot-metal charges was found to be 3 hr. This included a heating time of

$\frac{1}{2}$ - $\frac{3}{4}$  hr. before adding the metal. If good heavy scrap were available this time could be reduced, provided that adequate heating was carried out. If not, then shortly after adding the metal foaming was experienced and no gain in the charge time resulted.

Some of the 52-57% hot-metal charges have been analysed in Figs. B, C, and D. Fig. B shows the frequency of charging times and Fig. C how the frequency of charge-to-tap time varied for four ranges of charging time; the maxima on these curves have then been taken off and plotted in Fig. D to show the relation between charge-to-tap and charging times. The optimum charging time thus appears to be 3- $\frac{3}{4}$  hr. This last curve shows how the heat time increases more rapidly as the charging time becomes extended.

When the methane content of the coke-oven gas is low, in the region of 25%, the flame is extremely light, and an influx of large amounts of air through the front lining is apt to occur. If a mixed-gas furnace works with excessive draught, roof troubles will become apparent; the flame travels over to the back of the furnace and up the back wall to

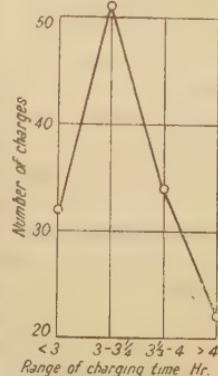


FIG. B.—Frequency Curve of Charging Times.

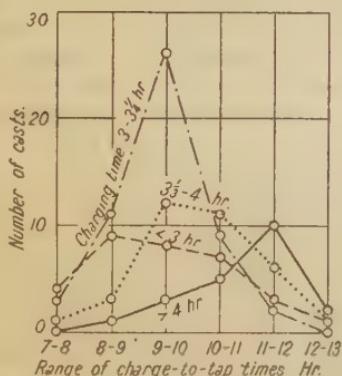


FIG. C.—Frequency Curves of Charge-to-Tap Times for four ranges of charging times.

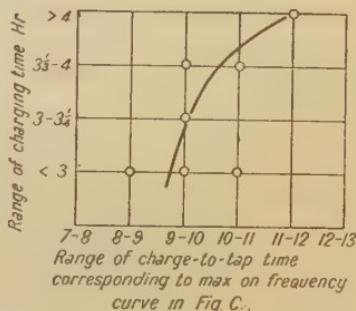


FIG. D.—Relation between Charge-to-Tap and Charging Times.

the roof. With a modern design of straight-through flues a stack draught of 1.2 in. W.G. should be the maximum required.

Dr. W. M. HAMPTON (Messrs. Chance Brothers, Ltd., Smethwick) wrote: As late Chairman of the Furnace Sub-Committee of the Society of Glass Technology, I have been asked to comment on the reference made in Dr. Leckie's paper to the performance figure for glass tanks. The Committee feel that the statement given is too abbreviated to do justice to the considerable amount of work

that has gone into this subject. The reference is admittedly to the original paper of which the present writer was author, but that did considerably more than provide an expression for the no-load heat consumption. The formula attempted was intended to provide far more than a simple no-load heat consumption, and the suggestion that a derivation by statistical methods would give the same result is incorrect, quite apart from the fact that to obtain statistically such information requires an inordinately long period of time. The essential feature was a new conception that the function of the heat supply of a glass tank furnace was to maintain a surface at a predetermined temperature, and a measure of thermal efficiency of a glass tank was the amount of heat needed for that purpose. It was, therefore, laid down that the performance should be related to the amount of heat needed per unit area of the tank at a defined temperature and under the no-load condition. Since it was also known that a higher efficiency was obtainable with a large furnace than with a small one, in order to be able to compare tanks of different sizes a size correction factor was essential. Based on the original paper by the present writer, the Committee have now, after the exploration of conditions in very many glass tank furnaces up and down the country, issued a standard formula, which has been adopted by the Society and full publication of which will appear in their *Journal* shortly. Contrary to the statement in the paper, neither this nor the original expression is complicated, although the derivation might possibly be so considered. The standard form finally accepted is expressed numerically by the number of B.Th.U. per second required to maintain 1 sq. ft. of the furnace area at 1400° C. under the no-load condition, reference being made to a furnace having a standard area of 600 sq. ft. In symbols this is :

$$Q = 0.026 \left( \frac{GH}{AK_A K_T} - \frac{Wc}{AK_A} \right)$$

where  $Q$  = Quantity of heat required per second to maintain 1 sq. ft. of furnace area at 1400° C. [B.Th.U. per sq. ft. per sec.]

$G$  = Total quantity of fuel consumed in furnace. [Tons per 24 hr.]

$H$  = Net heat contents of the main fuel as supplied : (a) in the case of producer gas, to the reversing valve of the furnace system, (b) in the case of coke-oven gas, natural gas or liquid fuel, to the burner. [B.Th.U. per lb.]

$A$  = Total area of melting and working portions of the furnace, exposed to the crown when the furnace is new. [Sq. ft.]

$W$  = Weight of glass discharged from the furnace per 24 hr. [Tons per 24 hr.]

$c$  = Quantity of heat required, at the reversing valve of the furnace system or at an equivalent position, for melting the raw materials needed to yield 1 lb. of glass and to raise the temperature of the glass to 1400° C. [B.Th.U. per lb.]

$K_T$  = Correction factor to be applied when the furnace, as a whole, is working at some temperature other than 1400° C.

$K_A$  = Factor to enable correction of furnace area to be made to the standard of 600 sq. ft.

Tables are provided for the values of  $K_T$  and  $K_A$ .

Sufficient experience has been obtained during the last two years on the application of this formula to existing furnaces to demonstrate its value both as a means of comparing one furnace with another and for controlling the performance of a furnace during a run. An early result of its use has been to confirm what has been shown previously without the use of the formula, namely, that there is a steady and progressive decrease in thermal performance with age, due partly to the solution of the side blocks and partly to the decrease in efficiency of the regenerators. In short, by the elimination, if in a somewhat arbitrary manner, of known important variables it has been possible to concentrate on the residual effects, and in several cases it has become possible to obtain a marked decrease in fuel consumption by the modification of factors of which the very existence was previously hidden by other factors over which the operator had no direct control.

Mr. A. STIRLING (London) wrote : Since Dr. Leckie's admirable paper advances appreciation of the relationship existing between the quantities  $h$ ,  $h_0$  and  $(h - h_0)/h$  by reference to specific examples, it may be of interest to append some calculated values of the ideal efficiency of the open-hearth furnace.

The ideal efficiency ( $E_T$ ) may be defined as the difference in heat contents of a unit volume of combustion gases on their generation and discard from the furnace laboratory expressed as a percentage of the heat content of the combustion gases on their generation.

Let :

$H$  = Net calorific value of fuel gas. B.Th.U. per cu. ft. at  $0^\circ$  C.,  
760 mm. Hg, dry (n. cu. ft.).

$A_0$  = Theoretical combustion air requirement. N. cu. ft. per n. cu. ft.

$V_0$  = Theoretical combustion gas volume. N. cu. ft. per n. cu. ft.

$n$  = Ratio of air supply  $A$  to theoretical,  $A_0$ .

$V$  = Actual combustion gas volume. N. cu. ft. per n. cu. ft.

$= V_0 + (n - 1)A_0$ .

$i$  = Heat content of combustion gases on generation. B.Th.U. per n. cu. ft.

$$= \frac{H}{V_0 + (n - 1)A_0}.$$

$i_a$  = Heat content of combustion gases due to air preheated to  $t_a$ ° C.  
B.Th.U. per n. cu. ft.

$i_g$  = Heat content of combustion gases due to gas preheated to  $t_g$ ° C.  
B.Th.U. per n. cu. ft.

$I$  = Total heat content of combustion gases. B.Th.U. per n. cu. ft.  
 $= i + i_a + i_g$ .

$i_d$  = Heat content of combustion gases leaving furnace laboratory at  
 $t_d$ ° C. B.Th.U. per n. cu. ft.

Whence :

$$E_T = \frac{I - i_d}{I} 100.$$

TABLE A.—*Ideal Thermal Efficiencies of Open-Hearth Furnaces.*

(a) $H = 140$ ; $t_a = 1100$ ; $t_g = 1100$ ; $t_d = 1550$ .													
$n$	.	.	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$i$	.	.	73.6	70.0	66.0	62.8	60.0	57.1	54.9	52.1	50.2	48.3	46.9
$i_a$	.	.	23.9	25.0	26.1	26.6	27.3	28.1	28.6	29.2	29.9	30.1	30.7
$i_g$	.	.	21.5	20.7	19.3	18.6	17.6	16.8	16.1	15.7	15.0	14.3	13.8
$I$	.	.	119.0	115.7	111.4	108.0	104.9	102.0	99.6	97.0	95.1	92.7	91.4
$i_d$	.	.	68.5	68.2	67.8	67.5	67.2	66.9	66.6	66.3	66.0	65.8	65.5
$I - i_d$	.	.	50.5	47.5	43.6	40.5	37.7	35.1	33.3	30.7	29.1	26.9	25.9
$I - i_d$ %	.	.	42.4	41.4	39.2	37.5	36.0	34.4	33.3	31.6	30.6	29.0	28.3
$I$													
$I - i_d$ %	.	.	68.6	67.9	66.0	64.5	62.9	61.4	60.7	58.9	58.0	55.7	55.2
(b) $H = 140$ ; $t_a = 1200$ ; $t_a = 1000$ ; $t_d = 1550$ .													
$n$	.	.	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$i$	.	.	73.6	70.0	66.0	62.8	60.0	57.1	54.9	52.1	50.2	48.3	46.9
$i_a$	.	.	26.1	27.2	28.3	29.1	30.1	30.9	31.4	32.0	32.3	33.0	33.3
$i_g$	.	.	19.8	18.7	17.8	16.9	16.0	15.2	14.6	14.0	13.5	12.9	12.5
$I$	.	.	119.5	115.9	112.1	108.8	106.1	103.2	100.9	98.1	96.0	94.2	92.7
$i_d$	.	.	68.5	68.2	67.8	67.5	67.2	66.9	66.6	66.3	66.0	65.8	65.5
$I - i_d$	.	.	51.0	47.7	44.3	41.3	38.9	36.3	34.3	31.8	30.0	28.4	27.2
$I - i_d$ %	.	.	42.6	41.2	39.5	38.0	36.6	35.2	34.0	32.4	31.3	30.2	29.4
$I$													
$I - i_d$ %	.	.	69.3	68.1	67.1	65.8	64.9	63.5	62.5	61.0	59.8	58.9	58.0
(c) $H = 150$ ; $t_a = 1100$ ; $t_g = 1100$ ; $t_d = 1550$ .													
$n$	.	.	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$i$	.	.	76.0	71.8	68.0	64.8	61.5	58.6	55.8	53.7	51.6	49.8	48.0
$i_a$	.	.	24.9	25.9	26.7	27.4	28.0	28.8	29.4	29.8	30.2	30.7	31.1
$i_g$	.	.	21.1	19.9	18.9	18.0	17.0	16.3	15.6	14.9	14.2	13.8	13.2
$I$	.	.	122.0	117.6	113.6	110.2	106.5	103.7	100.8	98.4	96.0	94.3	92.3
$i_d$	.	.	68.5	68.2	67.8	67.5	67.2	66.9	66.6	66.3	66.0	65.8	65.5
$I - i_d$	.	.	53.5	49.4	45.8	42.7	39.3	36.8	34.2	32.1	30.0	28.5	26.8
$I - i_d$ %	.	.	43.8	42.0	40.4	38.8	36.9	35.4	34.0	32.6	31.2	30.2	29.0
$I$													
$I - i_d$ %	.	.	70.4	68.7	67.5	65.8	63.9	62.6	61.3	59.8	58.1	57.1	55.9
(d) $H = 150$ ; $t_a = 1200$ ; $t_g = 1000$ ; $t_d = 1550$ .													
$n$	.	.	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$i$	.	.	76.0	71.8	68.0	64.8	61.5	58.5	55.8	53.7	51.6	49.8	48.0
$i_a$	.	.	27.3	28.3	29.5	30.1	31.0	31.8	32.4	32.9	33.4	33.9	34.3
$i_g$	.	.	19.1	17.9	16.9	16.1	15.3	14.7	14.0	13.3	12.9	12.4	12.0
$I$	.	.	122.4	118.0	114.4	111.0	107.8	105.0	102.2	99.9	97.9	96.1	94.3
$i_d$	.	.	68.5	68.2	67.8	67.5	67.2	66.9	66.6	66.3	66.0	65.8	65.5
$I - i_d$	.	.	53.9	49.8	46.6	43.5	40.6	38.1	35.6	33.6	31.9	30.3	28.8
$I - i_d$ %	.	.	44.0	42.3	40.7	39.2	37.4	36.2	34.8	33.7	32.6	31.5	30.6
$I$													
$I - i_d$ %	.	.	71.0	69.4	68.5	67.0	66.0	64.9	63.7	62.5	61.8	60.7	60.0

Table A gives values of  $\frac{I - i_d}{I} \times 100$  over the range from theoretical combustions to combustion with 100% of excess air for two calorific values and, for each, for two conditions of gas and air preheat. They illustrate that :

(a) In the range of calorific value considered, higher ideal efficiencies are obtained with the higher-calorific-value gas.

(b) For each of the two gases higher ideal efficiencies are obtained with the higher air-preheat conditions.

(c) For each of the two gases and each condition of preheat ideal efficiencies decrease with increasing excess air.

(d) For each of the two gases the decrease of ideal efficiency with increasing excess air is less at the higher air preheat than at the lower.

(e) For each of the two gases the combined heat content of gas and combustion air (relative to unit volume of combustion gases) from preheat decreases appreciably with increasing excess air at the lower air preheat but remains practically constant at the higher air preheat.

(f) For each of the two gases the combined heat content of gas and combustion air (relative to unit volume of combustion gases) is higher at the higher air preheat than at the lower, the difference increasing with increasing excess air.

As tables of the above type assist the ready and rapid assessment of the quantitative significance of changes in operating conditions arising from producer operation, regenerator working and combustion conditions, their preparation in a series covering the operating conditions likely to arise would prove a useful adjunct to process control.

It may be noted that the quantity of heat given up in the furnace, i.e.:

$$\text{or } \frac{(I - i_d)}{V} \quad \text{B.Th.U. per n. cu. ft. of combustion gas}$$

$$\frac{(I - i_d)V}{V} \quad \text{B.Th.U. per n. cu. ft. of fuel gas,}$$

can be related to the fuel-gas calorific value,  $H$ , in the ratio :

$$\frac{(I - i_d)}{H} V,$$

or, since  $i = \frac{H}{V}$  by definition,

$$\text{as } \frac{I - i_d}{i}.$$

This ratio expressed as a percentage is an index of the useful calorific value of the fuel, and is included in Table A.

It is hoped that no confusion will arise in the use of the symbol  $H$  in the paper and these remarks. The recurrence, if unfortunate, has been allowed to remain to preserve the Rosin-Fehling notation used above, since the  $IT$  diagram of these authors has been used in the combustion calculations made. In this connection two points of detail may be mentioned : First, that the values of the heat content of preheated air measured above  $0^\circ \text{C}$ . calculated by Dr. Leckie from Spiers' data are somewhat higher than those used by Dr. Rosin and Dr. Fehling in the  $IT$  diagram and related charts, and secondly that throughout Table A the writer has used the same value of  $i_d$  for a given value of  $n$  at both the higher and lower calorific values. Whilst it is realised that this is not strictly correct, and that the change is greater among lean gases than rich gases, it is believed that no appreciable misconception is introduced

through this expression of a practical difficulty sometimes encountered in using the valuable Rosin-Fehling charts in the reproductions ordinarily available in British units.

#### AUTHORS' REPLIES.

Mr. EVANS wrote in reply : Before answering the various points raised I would like to thank all those who have taken part in the discussion, and who have thereby greatly enhanced the value of the paper. It is particularly gratifying to note that men of experience in our iron and steel industry have, in general, agreed with the views expressed.

This paper did not set out to condemn mixed-gas firing as a process to be forgiven and forgotten. On p. 416 P of the paper the following words occur : "If the coke-oven gas is rich in methane and heavy hydrocarbons, the regeneration of a blast-furnace gas and coke-oven gas mixture is as efficient and economical, so far as steelmaking is concerned, as any other method of firing. Where, however, the coke-oven gas is of a lean nature, containing less than 27% of methane with a normal heavy hydrocarbon content, tar must be used as an artificial illuminant." This is the pith of the matter, and, whilst it is known that several works are using mixed gases successfully without tar, they are able to do this because their coke-oven gas is rich and of a high calorific value. It is when the lean nature of the coke-oven gas necessitates the use of an added illuminant that difficulties arise.

Mr. Robinson's remarks are appreciated. I have noticed the existence of an aura of hydrogen round the mixed-gas flame. If the gas port is in good shape, the flame comes well down on the charge and does not appear to attack the roof unduly. If, however, the port is worn and, as a result, the flame rides high, particularly after the middle door, the attack on the roof, though slow, is persistent, although the flame does not appear to touch the roof. This effect is even more pronounced at the outgoing port, which, under certain circumstances, is severely attacked, even though the flame is relatively short. These facts certainly suggest that there is an "aura" or "area of destruction" round the flame which has no visible characteristics. The effect has been noticed particularly in straight coke-oven-gas furnaces and is not entirely absent in producer-gas flames. It seems likely that the destructive effect is due more to very hot water vapour than to hydrogen.

With regard to the suggestion that very quick combustion results in short flames which are not always desirable, I agree with Mr. Robinson up to a point. No doubt rapid combustion tends to shorten the flame, but it is a very hot and quick-melting flame, which should be advantageous for high-scrap charges. In furnaces

designed to produce such rapid combustion the flame may be lengthened if desired by a reduction in the air input; in large tilting furnaces using high-iron and low-scrap charges, there is not the same necessity for such high calorific intensity as is the case in fixed furnaces using high-scrap and low-iron charges.

I am indebted to Mr. Kilby for his emphasis on certain paragraphs of the paper. The education of the melter to operate according to a battery of dials and charts is no small part of the responsibility incurred by the management during a change-over from producer to mixed gases. In the change-over reviewed in the paper, which also included a new valve system and completely new reversing arrangements, after a full explanation of the theory to the men (in two lectures) remarkably little trouble was experienced, and the men became "instrument-minded" quickly and with enthusiasm.

Mr. Kilby is well qualified to speak on the advantages of using cold coke-oven gas and tar; I was interested to hear details of his own experience, which confirm my views.

In the last paragraph of the paper, quoted by Mr. Kilby, I had in mind the comparison of a furnace operated on mixed gases with one operated on cold coke-oven gas and tar; I believe that in the latter method, with its preservation of flame direction, constancy of value of the thermal input and lack of foaming, the management would find more time to devote to other aspects of steel manufacture than when using mixed gases.

Undoubtedly the quality of the iron charged does affect the tendency to foam. High-silicon iron, which produces in the initial stages a high-silica slag, generally increases the foaming tendency, which is not decreased by the probability of a resulting hard melt.

I was very interested to hear from Mr. Hacking that, in order to cut down water-cooling losses, he was modifying the ports of his Hoesch furnaces. This is a progressive step which I hope will be successful; the water consumption on these furnaces is undoubtedly heavy, and any steps taken to decrease the heat losses are deserving of success. I wholeheartedly agree with Mr. Hacking that in orthodox designs of furnaces the gas-port shape has probably a greater effect on the speed and efficiency of the furnace working than all other factors combined. As soon as the gas port starts to lose its shape away go all the thought and care expended on its design and building. As Mr. Hacking observes, this cannot possibly happen with water-cooled gas burners and tar injectors. I would hazard a forecast that the days of the orthodox gas port and gas regenerators are numbered and that post-war development will record a major improvement due to this.

I must thank Dr. Colclough for his contribution. His figures of heat consumption for furnaces using low-grade residues show what can be achieved on large modern furnaces; this should stimulate the serious consideration of this type of furnace by

those who contemplate the erection of new plant. Dr. Colclough also rightly stresses the considerable reduction in capital expenditure which the elimination of gas producers, gas regenerators, &c., will entail.

Mr. Whiteley has raised points which are very pertinent in the sphere of mixed-gas practice. It can be stated quite definitely that a reduction in the calorific value of the gas from, say, 220 to 175 B.Th.U. per cu. ft. will not succeed in subduing the foam. Such a reduction in the calorific value must be effected by reducing the proportion of coke-oven gas in the mixture. If it were done by reducing the blast-furnace-gas proportion, the reduction in total volume passing through the gas port would be such that the gas velocity would be too drastically reduced. When the amount of coke-oven gas is reduced, so also are the luminosity-producing constituents, which results in less flame luminosity and no decrease in foam.

It is our opinion that the steel is not affected in any way by the use of mixed gases, and we are in a good position to judge this, having one shop on producer and one on mixed gas, both shops serving the same plate and section mills. We can also state that we very rarely see a hair-line crack in steel from either shop.

Although I have had no experience of mixed gases in an acid furnace, I am of the opinion that the tendency to foam would be greater in such a furnace, owing to the increased silica in the slag.

On the question of buoyancy of hydrogen in the flame, I do not believe that much stratification is possible. The gas is injected into the furnace at high velocity and burns quickly and turbulently. The products of combustion, water vapour and CO<sub>2</sub>, may then reasonably be expected to be equally diffused through the flame. Owing to turbulence, I cannot believe that the "stay time" of the flame in the furnace would permit of stratification.

I agree with Mr. Thring, in general, that any means of imparting more heat to the charge than to the roof is of the greatest importance, but I doubt whether the use of a relatively opaque flame, so arranged as to be hotter at its inside than at its top, is actually a practical solution; the use of an opaque flame, *i.e.*, a highly luminous flame, is at all times desirable. I believe that one of the reasons why a flame in the open-hearth furnace tends to be cooler underneath is that at that point it is less accessible to oxygen, owing to the introduction of the air above the gas.

The heat-flow meter referred to by Mr. Thring is useful and should be of value to open-hearth operators in assessing the radiation properties of their flames; steelworkers will be glad to hear more of this.

I wish to thank Mr. Pearson for his interesting and useful contribution to the discussion. I quite agree with him when he says: "With regard to flame characteristics, in the absence of absolute experimental data, much must be conjectural." This indicates the

great necessity for experimental research into all aspects of flame radiation, so that our knowledge of this very important subject may be converted from "conjectural" into "definite."

I also believe the axiom that "all slags have the ability to foam"; this can be most surely demonstrated in the Hoesch furnace with a completely non-luminous coke-oven-gas flame, where one has only to arrange for a charge to melt out slightly hard in order to guarantee a foaming slag.

As, however, the foaming slag can be just as easily converted into a normal slag, and that right quickly by the introduction of an illuminant, it seems logical to assume that of the two tendencies:

- (a) The tendency of the slag to foam, and
- (b) the tendency of the flame to inhibit the foam,

the latter is considerably more powerful than the former, *i.e.*, the flame character has considerably more effect in suppressing the foam than any characteristic that the slag may possess which induces it.

Again, in the Hoesch furnace the flame is so devoid of luminosity that it is absolutely invisible in the furnace. This flame, however, owing to its high temperature, melts a charge very fast, and such melting is carried out by convection and conduction, not by radiation; the furnace itself is raised to very high temperatures under these conditions. It seems difficult then to reconcile any tendency which the slag has to foam with lack of heat under these conditions. The endothermic reactions to which Mr. Pearson refers surely occur to the same extent in producer-gas-fired furnaces, which foam to a much less degree.

I cannot agree with Mr. Pearson when he argues that the heat of the flame must be dissipated quickly because carbon dioxide and water vapour radiate with the speed of light; that they do so is well known, but first of all they have to be formed by combustion, and it is during this process that the great build-up of heat occurs, causing an increase in temperature. Wherever there is flame, there also is combustion, and if all the heat generated by combustion were immediately radiated there would be no flame temperature. The answer is that even with a fully luminous flame (*i.e.*, a flame infinitely thick) the total radiation from water vapour is only about 16% and for carbon dioxide about 10% of black-body radiation at furnace temperatures; but with ordinary flame dimensions this maximum is seldom approached, so that even if the water vapour and CO<sub>2</sub> radiated with infinitely high velocity they would still not radiate a sufficiently high proportion of the total heat released by combustion to prevent the rise in temperature. When I said "the great evolution of heat in the flame cannot be dissipated quickly enough" I referred to the quantity of heat dissipated per unit of time, not to the linear speed with which it travelled away from the flame.

With regard to instruments, the tar meters in use on our furnaces are Kent tar and heavy-oil flowmeters: these instruments indicate the rate of flow by the speed at which a needle moves over a circular dial marked in gallons of fuel. Thus the movement of the needle has to be timed, which is quite a simple operation. It also totals the amount of fuel used.

The value of temperature indicators in the blast-furnace and coke-oven gas mains lies in their ability to point to a source of loss of luminosity and the accompanying increased slag foaming, which might otherwise be attributed to some other unknown cause, the attempted tracing of which would involve both time and worry.

I was interested to note Mr. Evans' frequency curves which give definite information on the effect of different proportions of hot metal. Nevertheless, Mr. Evans has not mentioned some factors which have a considerable bearing on these proportions. The most important of these is the ratio of blast-furnace to coke-oven gas, which I stipulated should be 2 : 1. If higher proportions of the latter gas are used, no doubt higher proportions of hot metal can be carried. The question of slagging also is important; if slag can be got rid of at all, during any part of the operation, this is an advantage. Further, the maximum percentages of hot metal given in the paper were those which could "conveniently be carried." We have used higher proportions of hot metal than the indicated maximum without much loss of time, but in general the furnace structures suffered.

I do not agree that "tar cannot give the same efficient luminosity as high preheats." American furnaces using pitch, tar or heavy-oil residues only are giving very high rates of production with extremely low fuel consumptions; the rate of heat transfer, I suggest, on these furnaces is far higher than anything which can be obtained in mixed-gas furnaces. Also, among the great advantages claimed for tar firing is the preservation of the flame direction throughout the campaign.

I think it likely that the introduction of tar at the entrance to the gas regenerators, apart from practical difficulties, would lead to early sooting of the checkerwork.

Dr. LECKIE replied: I should like to thank the contributors to the discussion and correspondence, which will be very helpful in further work on the subject.

One could agree with Mr. Robinson's suggestion that it would be of interest to construct similar characteristic curves for the furnace as a whole, including the checkers. I feel, however, that, since the main object of the method is to elucidate the effect of alterations in the design of the melting chamber on the performance, to include the checkers, flues and valves might lead to a masking of the effect of, say, modification of port design or of roof contour. For this reason the calculations were restricted to conditions in the upper part of the furnace.

The point of optimum operation, whether  $BB'$  or  $CC'$ , would depend on the plant, on the process and on the prevailing economic conditions. Mr. Robinson drew attention to the very important point that it was not weekly output but long-period output (including repair periods) which was the governing factor.

In the calculation of  $H$  it is possible to introduce refinements to allow for the heat requirement of fettling materials and for the temperature of the hot metal. The quantities normally involved are, however, small compared with the variations due to the different charge compositions, and, whilst it would doubtless be preferable to include all possible variations, the extra work involved if some hundred or so values of  $H$  had to be calculated would be considerable, and would not be likely to alter appreciably the resulting curves. The same argument could also be applied to attempts to calculate  $k$  more accurately. The extent to which these refinements could be applied would naturally depend on the computing staff available; it must be remembered that the methods proposed are not intended primarily for fundamental research purposes but for works use on a wider scale.

Dr. Binnie drew attention to a discrepancy in the relative slopes of the curves in Fig. 5 of my paper. When preparing these curves the basic points, even when calculated from large group-averages, are bound to show a small scatter, and it is not always easy to see the extent of curvature, if this is slight. To draw the best curves through the points according to accepted statistical methods would (in the absence of a completely equipped statistical laboratory) make impossible demands on the staff doing the calculations. However, it is always possible to see when a furnace is being worked beyond the optimum ( $CC'$  of Fig. 1), though in other cases there might be more doubt as to whether the curve were in the region of  $BB'-CC'$  or not. In Fig. 5, from the trend of the  $RR'$  (top) curve, it is clear that there should be slight curvature on the other lines, as Dr. Binnie suggested.

Usually the points for the  $PP'$  ( $h_o$ ) line show the least scatter, and this perhaps could be used as the best guide to the slope of the other curves. If  $PP'$  were a straight line of slope less than  $45^\circ$  the  $AA'-BB'$  region would be involved. In the  $BB'-CC'$  region  $PP'$  would show curvature, gradually increasing to a slope of  $45^\circ$ , and the slope would be exactly  $45^\circ$  at  $CC'$ . A slope of the  $PP'$  curve greater than  $45^\circ$  would indicate a negative slope of the  $QQ'$  curve as in the region beyond  $CC'$ .<sup>1</sup>

With regard to the air/gas ratios in Fig. 7, the air and gas volumes were as metered. It seemed that without pressure control in the melting chamber high air/gas ratios were desirable. Although, as Dr. Binnie said, extra sensible heat can be carried away by the excess air, this preheated excess air either improves combustion or else leads to decreased infiltration of non-preheated air to an

<sup>1</sup> These relationships can be simply proved mathematically by considering the signs of the differentials concerned.

extent which more than compensates for the additional waste-gas loss.

Mr. Hacking's offer to supply statistics for some of his furnaces provided with gas meters is welcomed.

With regard to Dr. Hampton's communication, I feel that an apology is due to him if the remarks in the present paper could be taken to mean that the formula of the Society of Glass Technology Committee was of little interest to steel-furnace technologists. This formula merits full study, and it was assumed that all those concerned in the investigation of heat-transfer problems would read Dr. Hampton's original paper.

The formula given in Dr. Hampton's communication defines the heat necessary to maintain 1 sq. ft. of the furnace area at 1400° C. under no-load conditions, with corrective factors for furnace size and temperature to bring all units to a common basis. The area referred to is the surface of the molten glass in a full tank. Since glass tanks operate continuously, as distinct from steel furnaces which operate a "batch process," the standard surface area is always maintained, and application of the formula is straightforward. It would be difficult to adapt this to a steel furnace, as a standard area could not well be established. The only time when conditions in a glass tank are simulated is when the bath is flat, and at this period a considerable and indeterminate amount of chemical heat is always produced which would vitiate the conclusions.

I feel that with glass furnaces, where conditions are much more stable, a standard formula can give results quickly, the relative stability of the conditions making the application of statistical methods less appropriate. The converse applies to steel furnaces, where the large number of variables makes the statistical approach preferable.

Mr. Stirling raised a point of the utmost importance—the maximum efficiency which could be obtained with a furnace in which the gases left the operating chamber at a temperature of 1500–1600° C. His calculations show that with the air/gas ratios usually encountered the "ideal efficiency" (taking preheat into account) is 26–36%. This ideal efficiency does not include the radiation loss, which would somewhat diminish the value, so that the maximum efficiency theoretically obtainable would be less than this. Yet the furnaces examined had melting-chamber efficiencies of 24–29%. It seems, therefore, that open-hearth furnaces operate much nearer to the maximum obtainable thermal efficiency than has been hitherto thought.

Incidentally, Mr. Stirling's Table A draws attention to the danger of taking the simple ratio of calorific values in considering the relative values of fuel gases. This Table should be carefully studied by operators contemplating changing furnace conditions.

# SURVEY OF LIQUID STEEL TEMPERATURES IN BASIC OPEN-HEARTH FURNACES.\*

By D. MANTERFIELD (MESSRS. STEEL, PEECH AND TOZER, SHEFFIELD).

*Paper No. 23/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Liquid Steel Temperature Sub-Committee).*

## SUMMARY.

Temperature surveys have already been made on acid open-hearth furnaces and electric furnaces by other investigators. The object of the present work was to continue these investigations by temperature explorations on the larger type of basic open-hearth furnaces.

In the first part of the paper details are given of the type of furnace and slag dealt with in the survey. Temperatures were taken by means of the Schofield-Grace quick-immersion pyrometer, using a portable type of potentiometer for measurement. Readings were taken at various positions in the vertical and horizontal plane, and the results are tabulated and discussed.

A point in the centre of the bath at a depth of 9 in. in the steel is the standard position for measurement. The mean deviation from this figure at all the positions explored was 5.5° C. (9.9° F.). It is concluded that a single temperature measured at the standard position can be taken as representative of the bath as a whole.

The uniformity of temperature in the bath is shown to be governed by its activity.

The second part of the paper concerns the temperature fluctuations during the progress of a heat. A series of typical time-temperature diagrams is given, with details of the furnace additions. These show only a very temporary depression of temperature due to such additions. At the beginning of the refining period an average superheat (over the melting point) of 40° C. (72° F.) prevails, rising to 70–100° C. (126–180° F.) at the going-on stage. The response of the metal to alteration in flame conditions is also discussed.

Finally a number of slag and metal temperatures was taken, the metal at the standard depth and the slag at a depth of 2 in. The results indicate that during the reaction period the activity equalises the temperature of both the slag and the metal. In the final stages of refining a greater difference was found. The slag temperatures were higher than the metal by from 1° C. (2° F.) to 47° C. (84° F.), depending upon the condition of the bath and the prevailing steel temperature.

## Introduction.

SURVEYS of temperature distribution in a number of types of furnace have already been carried out on acid open-hearth furnaces and various types of electric furnaces. Some details of preliminary work were published in the Second Report of the Liquid Steel Temperature Sub-Committee<sup>(1)</sup> and further details were given in the Third Report<sup>(2)</sup>

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of that Sub-Committee. Oliver and Land<sup>(3)</sup> considerably extended this work on the smaller acid open-hearth and four types of electric furnace. The subject was still further extended by Hatfield<sup>(4)</sup> in his contribution to the discussion on the latter paper.

The object of the present work was to continue this experimental work by temperature explorations in the larger type of basic open-hearth furnace. It was thought that the difference in the hearth and the slag composition and in the technique of the basic process might cause some variation at different stages of the process and at different positions in the bath.

Previous work by the author had already demonstrated the temperature variation with the carbon content of the steel. In addition, the physical and chemical properties of basic slags show some variation between high- and low-carbon charges. In consequence, an endeavour was made in the present survey to cover a number of different steel qualities. Temperature control was being exercised during the period covered by these investigations.

#### *Type of Furnace and Slag.*

The furnaces were 87-ton cold-charged basic open-hearts of fixed type, fired by producer gas. Coke-oven gas was available

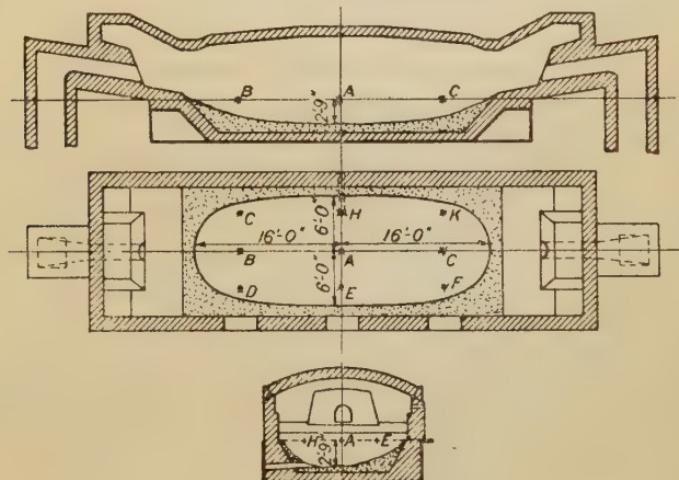


FIG. 1.—Typical Furnace, showing the positions explored.

for enrichment of the producer gas as and when required. The air and gas ports were as shown in Fig. 1 on all furnaces except one, which was of the Maerz type.

As stated in the Introduction, the type of slag varies somewhat with the steel composition. The slags on low-carbon charges are usually higher in FeO content than those on high-carbon charges, and their thermal conductivity would also vary in consequence.

The average slag thickness would be about 5 in., though slags up to 9 in. thick have been encountered. Some slag temperatures and time-temperature surveys are included in this investigation and reference is made to these in a later section.

A simplified diagram of a typical furnace, showing the positions explored, is given in Fig. 1.

#### *Apparatus and Procedure.*

Duplicate pyrometers of the Schofield-Grace quick-immersion type as described in previous Sub-Committee Reports were available for use. These are in operation for routine control, and all the tests were made under supervision and by experienced operatives.

The main arm of the couple is 15 ft. long, and the vertical portion is protected by the usual carbon end block which is necessary for basic slags. Approximately half the arm is protected by diatomite insulating blocks, and the rare-metal couple wires are taken to the cool end of the arm, whence compensating leads run to the potentiometer. With the large type of couple and for large furnaces a wheeled trolley is necessary, of which two were available.

To reach the positions near the back bank (*G*, *H* and *K*, Fig. 1) it was necessary to construct a special long arm. This was 21 ft. long and was protected for half its length by a paste of insulating cement and siliceous clay applied 1 in. thick. In addition, this carried a long carbon block (2 ft. long) to enable the tests at 18 in. deep to be taken without damage to the arm or insulation.

Three portable-type potentiometers were used for taking the measurements, and these have been found to be sensitive, stable and accurate.

Before commencing the tests, and several times during the period occupied by the investigation, these instruments were calibrated. They were also tried against each other by taking simultaneous and consecutive immersion readings, using alternate couples and potentiometers. The discrepancy was  $\pm 3^\circ$  C. ( $5^\circ$  F.) at most and usually  $\pm 2^\circ$  C. ( $3^\circ$  F.) or less.

New couples were used at the beginning of each experiment and renewed at least once during the course of each individual series. No couple used would thus have a total immersion time greater than 120 sec.

For several reasons it was decided to make the vertical and horizontal surveys separately. The normal silica sheath will not survive an immersion of more than 30 sec. and it would be difficult to take readings in three doors simultaneously. It was found difficult, too, to take readings near the front bank with the special long arm during preliminary tests. However, it was felt that the measurements at the standard depth (9 in.) during the vertical explorations could also be used in conjunction with the horizontal survey.

The positions at which immersions were made are shown in Fig. 1, positions *B*, *A* and *C* being on the longitudinal centre-line of the furnace and *E*, *A* and *H* on the transverse centre-line. The deepest part of the bath was 2 ft. 9 in. and was approximately at position *H*, just over the tap-hole. Owing to the slight slope of the bath from the front banks to this position, the greatest depth that could be safely achieved at positions *D*, *E* and *F* was 15 in., though one or two readings were taken at 18 in.

The procedure for the vertical survey, therefore, was to take measurements at two positions simultaneously at three depths with the special long arm and at two depths with the short arm. On withdrawal, the silica sheath on one instrument was quickly changed and the arm inserted in the third door. This could be done very quickly and there could be little or no change in temperature during the 2 min. which elapsed between the immersions. The long and short arms were used alternately at the different positions; hence, during the series of tests each position was explored on several occasions.

For the horizontal distribution the two shorter-arm instruments were used at a standard depth of 9 in. As these arms would not reach past the centre-line, positions *G*, *H* and *K* were not surveyed. Figures for these positions at 9 in. depth, for comparison with the centre-line positions *B*, *A* and *C*, are available in the vertical survey. The technique adopted here was to insert two instruments simultaneously and take temperatures at two positions. On withdrawal, the sheath was quickly changed and this machine used through the third door. This was alternated between the middle and each end door.

In the vertical survey some measurements were taken from the top downwards and others from the bottom upwards. Little or no difference could be found by the two procedures. In the horizontal tests, in some cases the middle-line positions were explored first and in others the positions near the front bank. Again little or no difference could be discovered in consequence.

The measurements were made at three stages, *viz.*, at melting, at going-on, and at tapping, and various furnaces and steel qualities were surveyed. Notes were made of the gas direction, bath condition and finishing additions. With the exception of finishing additions on two or three occasions, no measurements were taken after any bath additions until it was considered that sufficient time had elapsed for approximate equilibrium to be attained.

#### *Results of Temperature Survey.*

The details of the various tests are given in Tables I. and II., with a summary of the deviations in Table III.

These results are not strictly comparable with those of previous investigators, owing to the difference between the technique of the basic open-hearth process and that of the acid open-hearth or electric

TABLE I.—Vertical Distribution of Temperature in 87-ton Basic Open-Hearth Furnaces.

Exp. No.	Posi- tion.	Melted.			Going-on.			Carbon, %.	Tempera- ture.
		Depth, In.	Gas,	Bath Condition.	Position.	Depth, In.	Gas,		
1	H	9		o C.	o F.				
	H	18		1488	2710				
	H	24		1491	2716				
	A *	9		1493	2720				
	A	15	Left	1487	2709 *	Right	Boil subsiding.	0-13	1580 *
	G	9	to right.	"	"	to left.	Ready for tamping.	"	1564
	G	18	"	1501	2733	"	No finishing addi- tions to bath.	"	1583
	G	24	"	< 1450	26412	"	"	"	1589
			"	< 1450	26112	G	"	"	2876 *
			"	< 1450	26142	G	"	"	2847
2	A *	9		Just melted.	1535 *	2796 *	A *	9	1576
	A	15			1529	2781	A	9	2882
	K	9	Left		1528	2782	C	9	2876 *
	K	18	to right.		1523	2774	C	15	1583
	K	24	"		1492	2718	B	9	1589
	B	9	"		1561	2824	B	15	1609
	B	15	"		1543	2810	"	"	2869
			"				"	"	2912
			"				"	"	2936 *
			"				"	"	2909
3	A *	9		Good melt.	1508 *	2746 *	A *	9	1592
	A	15			1505	2740	A	15	1589
	H	9			1503	2737	H	9	1587
	H	18	Left		1503	2737	H	18	1587
	H	24	to right.		1499	2730	H	24	1587
	B	9	"		"	"	Right to left.	"	1587
	B	15	"		"	"	"	"	1587
	C	9	"		"	"	"	"	1587
	C	15	"		"	"	"	"	1587
			"		"	"	"	"	1587
4	A *	9		Just melted.	0-35	2804 *	A *	9	1586
	A	18	Left		"	1531	2788	A	1586
	H	9	to right.		"	1636	2796	H	9
	H	18	"		"	1534	2793	H	18
	H	24	"		"	1529	2784	H	24
			"					"	1587
			"					"	2833 *
			"					"	2831
			"					"	2831
			"					"	2831

\* Standard position.

TABLE II.—*Horizontal Distribution of Temperature in 87-ton Basic Open-Hearth Furnaces.*

All temperatures measured at a depth of 9 in.

Exp. No.	Posi- tion.	Melted.			Going-on.			Tapping.		
		Gas.	Bath Condition.	Carbon, %.	Gas.	Bath Condition.	Carbon, %.	Gas.	Bath Condition.	Carbon, %.
5	A *	Right to left.	"	0.23	Left to right.	7 min. after reversal.	0.16	Left * to right.	5 min. after reversal; no finishing to bath.	0.08
	B	Right to left.	Just melted.	0.23	1632 2790	1534 2794	1662 2845	1570 2858	1672 2862	1600 *
	C	Right to left.	"	0.23	1632 2790	1534 2794	1662 2845	1572 2858	1584 2844	1538
	D	Right to left.	"	0.23	1632 2790	1534 2794	1662 2845	1574 2859	1594 2901	2008
	E	Right to left.	"	0.23	1632 2790	1534 2794	1662 2845	1574 2859	1594 2901	2920
	F	Right to left.	"	0.23	1632 2790	1534 2794	1662 2845	1574 2859	1594 2901	2934
6	A *	Left to right.	Well melted.	1.01	1654 2837	1653 2837	1644 2831	1587 2889	1594 2901	1579 *
	B	Left to right.	Well melted.	1.01	1654 2837	1655 2831	1644 2829	1581 2878	1592 2887	2880
	C	Left to right.	Well melted.	1.01	1654 2837	1654 2831	1644 2829	1585 2904	1595 2904	2898
	D	Left to right.	Well melted.	1.01	1654 2837	1654 2831	1644 2829	1585 2904	1595 2904	2889
	F	Left to right.	Well melted.	1.01	1654 2837	1654 2831	1644 2829	1585 2904	1595 2904	2889
7	A *	Left to right.	Well melted.	1.25	1538 2786	1630 2786	1530 2804	1572 2872	1674 2872	1585 *
	B	Left to right.	Well melted.	1.25	1538 2786	1630 2786	1530 2804	1572 2872	1672 2862	2885
	C	Left to right.	Well melted.	1.25	1538 2786	1630 2786	1530 2804	1572 2872	1672 2862	2898
	D	Left to right.	Well melted.	1.25	1538 2786	1630 2786	1530 2804	1572 2872	1672 2862	2916
	E	Left to right.	Well melted.	1.25	1538 2786	1630 2786	1530 2804	1572 2872	1672 2862	2916
	F	Left to right.	Well melted.	1.25	1538 2786	1630 2786	1530 2804	1572 2872	1672 2862	2916
8	A *	"	"	"	"	"	"	"	"	2920
	B	"	"	"	"	"	"	"	"	2917
	C	"	"	"	"	"	"	"	"	2904
	D	"	"	"	"	"	"	"	"	2904
	E	"	"	"	"	"	"	"	"	2914
	F	"	"	"	"	"	"	"	"	2908

\* Standard position.

furnace. The usual procedure on the plant is to add the feed lime as soon as the charge is clear melted, followed by the necessary fluorspar addition. When this is fluxed the predetermined quantity of mill scale or ore is fed as quickly as the furnace will take it. From this point little or no further feed is necessary.

TABLE III.—*Summary of Temperature Deviations.*

Bath Condition.	Vertical.					Horizontal.				
	No.	Difference, Mean from Standard Position.	Max. Range at any One Position.	Average Range per Foot at any One Position.	Carbon, %.	No.	Difference, Mean from Standard Position.	Max. Range of All Positions.	Carbon, %.	
Melt.	1	° C. ° F. — 5° — 9°	° C. ° F. 14° 25°	° C. ° F. 12° 22°	0.63	5	° C. ° F. — 11° — 20°	° C. ° F. 36° 65°	0.29	
	2	+ 6 + 11	36 64	19 34	0.22	6	+ 3 + 5	11 20	1.01	
	3	0 0	4 7	6 11	1.50	7	+ 8 + 14	18 32	1.25	
	4	+ 6 + 11	9 16	9 16	0.35	8	... ...	... ...	...	
Going-on.	1	+ 3 + 5	16 29	18 32	0.13	5	— 8 — 14	32 57	0.16	
	2	+ 18 + 32	20 36	26 47	0.21	6	— 2 — 3	14 25	0.84	
	3	+ 2 + 3	4 7	2.5 4.5	0.75	7	+ 2 + 3	6 11	0.62	
	4	+ 2 + 3	9 16	7 12	0.13	8	... ...	... ...	...	
Tapping.	1	... ...	... ...	... ...	...	5	— 4 — 7	14 25	0.08	
	2	... ...	... ...	... ...	...	6 †	— 6 — 11	13 23	0.64	
	3	... ...	... ...	... ...	...	7 †	— 8 — 14	17 30	0.48	
	4	... ...	... ...	... ...	...	8 †	+ 1 + 2	27 49	0.08	

Mean Deviation of All Tests, Vertical and Horizontal, from the Standard Position:  
 Melt, 5.5° C. (9.9° F.).      Going-on, 5.8° C. (9.6° F.).      Tapping, 5.8° C. (10.4° F.).

\* Excluding G position.

† After finishing additions.

Nevertheless, the tests yield ample confirmation of the conclusions reached by Oliver and Land<sup>(3)</sup> and by Hatfield.<sup>(4)</sup> In addition, one or two other interesting points were indicated.

When the bath is uniformly active the spread of results is comparatively small. The carbon content of the steel in conjunction with the temperature and the slag condition will be an indication of the vigour of the boil. Carbon figures are given in Tables I., II., and III., and it will be seen that the range of temperature measurements bears some relationship to the figures quoted.

With the exception of tests 2 and 5 (low-carbon melts) the temperature taken at the standard position was in remarkable agreement with the mean of all temperatures in the individual survey. Of the 18 individual tests taken, no fewer than 14 were within  $\pm 6^\circ$  C. (11° F.) and 9 were within  $\pm 3^\circ$  C. (5° F.). Of the four which exceeded  $\pm 6^\circ$  C. (11° F.), three were on the lower-carbon melts and one was after the addition of finishings.

The mean deviation on all the tests was 5.5° C. (9.9° F.). A single measurement made at the standard position can therefore be taken as a representative figure for the bath. This is very gratifying

from the viewpoint of temperature control in practice. Furthermore, this gives added confidence in the use of such temperatures for physico-chemical investigations.

In the vertical explorations the temperature naturally decreases with the depth. The maximum temperature gradient in the present series is  $26^{\circ}$  C. ( $47^{\circ}$  F.) per foot; this was in test 2, where the bath conditions were obviously abnormal. The average gradient of the tests in the vertical survey is  $12.5^{\circ}$  C. ( $22^{\circ}$  F.) per foot; excluding No. 2, however, the average is  $9^{\circ}$  C. ( $16^{\circ}$  F.) per foot. This gradient will vary in different furnaces with the thermal conductivity of the hearth, *i.e.*, with the type, thickness and insulation.

In the horizontal distribution there is a wider range than was anticipated. There is a definite tendency for the bath at 9 in. depth to be hotter at the gas inlet than at the gas outlet. This would vary with the pitch, velocity, length and direction of the flame and with the type and thickness of the slag. It will be noted that in tests 3, 6 and 7, which would carry thicker and more viscous slags, there is little difference between the two ends. In the remainder of the tests the gas end averages approximately  $10^{\circ}$  C. ( $18^{\circ}$  F.) hotter than the other end.

In the majority of the observations the temperature of the bath was rather higher near the front bank than at the centre. Oliver and Land<sup>(3)</sup> had noted the tendency for the edges of the bath to be hotter than the centre, but the present survey showed this only at the front bank. This may be due to the front bank being rather thicker than the back, but the flame also had an influence in some cases, as in test 5 which shows the greatest increase; here the gas was fanning towards the front lining, and the hottest points were at the tail end of the flame. It will be noted that in this respect the higher-carbon baths (with more viscous slags) had the least temperature variation.

The deviation of the standard temperature measurement from the mean of all other positions showed little or no difference at the three stages of the refining process.

Immediately prior to the melt considerable variations will obviously occur, as shown in experiment No. 1. These variations are rapidly reduced as the bath becomes fully melted.

At the going-on stage the uniformity depends upon the activity of the bath and the effect of the flame.

After normal finishing additions this uniformity was quickly restored, provided that sufficient carbon was present to agitate the bath. Test 8, with very low carbon, had a range of  $27^{\circ}$  C. ( $49^{\circ}$  F.) 5 min. after the addition of 10 cwt. of ferro-manganese.

No opportunity occurred during the tests to take measurements after the bath had been quiescent for a sufficiently long period to investigate temperature gradients under these conditions.

*Fluctuations of Temperature During Refining.*

A series of time-temperature observations was made to investigate the temperature variations during the refining process due to bath additions.

A number of the curves giving the essential details are reproduced in Fig. 2.

It is apparent that only a relatively small degree of superheat is necessary in the basic open-hearth for the reactions to proceed satisfactorily. Calculations of the melting point of the metal before commencing to feed indicate that the bath was approximately 40° C. (72° F.) above its freezing point at this stage.

The earlier tests (Nos. 9, 10 and 11) indicated a steady increase in temperature during the reaction period after sufficient time had elapsed for the bath additions to work through. This was followed by a steeper rate of increase towards the tapping stage. It is necessary to have 70–100° C. (126–180° F.) of superheat at the finishing period to compensate for the cooling in the ladle and the tundish and during teeming.

In tests 12, 13 and 14 temperature measurements were taken as soon as possible after the additions of lime or scale to indicate the depression due to these materials. It appears that this decrease is very temporary and varies with the activity of the bath. No. 12, at 0.77% of carbon, had a feed of 2 tons of lime; 15 min. after this addition the temperature was 1° C. (2° F.) higher. No. 13, at 0.16% of carbon, had 55 cwt. of lime, and a measurement taken 15 min. later showed a decrease of 18° C. (32° F.).

In test 14 there was a decrease in temperature of 20° C. (36° F.) 13 min. after a feed of 38 cwt. of ore and mill scale. This was followed by an increase of 36° C. (65° F.) in 18 min.

The response of the metal to an alteration in the flame conditions is shown in test 10. With gas off for 10 min. and slow gas for 10 min. the temperature decreased 22° C. (40° F.). Earlier tests on acid open-hearth furnaces had also indicated a fall in temperature of 1° C. (2° F.) per min. with the gas off.

Earlier work on acid open-hearths with 55–60-ton charges had indicated a reduction of 1.3° C. (2.3° F.) per cwt. of finishing additions (with the exception of large additions of ferro-silicon). In the present series, with 87-ton charges in basic furnaces, Nos. 10 and 14 showed a decrease of 6° C. (11° F.) and 8° C. (14° F.), respectively, after the addition of 15 cwt. of finishing materials.

It is suggested that full thermal control of the refining reactions would necessitate a number of temperature measurements during the refining periods.

*Slag Temperatures.*

An investigation was also conducted on the relative slag and metal temperatures.

It was necessary to replace the silica sheath by a graphite sheath

for use with basic slags. Preliminary experiments gave steel temperatures 10–15° C. (18–27° F.) lower with a graphite sheath than with a silica sheath. By inserting a sillimanite ring between the carbon sheath and the carbon end block comparable results were obtained within  $\pm 3^\circ$  C. (5° F.), taking simultaneous measurements with each type. These were repeated a number of times

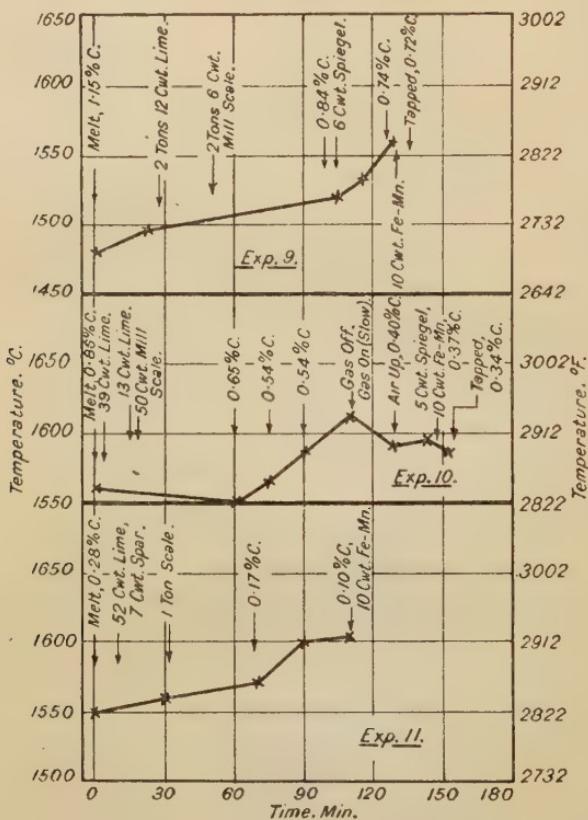


FIG. 2A (see Fig. 2B).—Temperature Variations during the Refining Process due to Bath Additions.

before commencing the series of slag temperature measurements to confirm the accuracy of the results. In some of the later experiments a small-bore silica sheath was also inserted inside the carbon sheath to ensure that the couple wires could not touch the carbon sheath.

The temperature measurements on the slag were taken at a depth of 2 in. and on the metal at the standard depth of 9 in. The details of the tests are given in Table IV.

During the reaction period the activity of the bath equalises the temperature of both the metal and slag, as indicated in experi-

ment 15. At three stages during this period the greatest difference was  $7^{\circ}$  C. ( $12^{\circ}$  F.). As the depths of the two points at which measurements were taken differed by 11 in. this shows a very small temperature gradient.

Towards the end of the refining process the slag and metal temperatures differed to a much greater extent. This difference

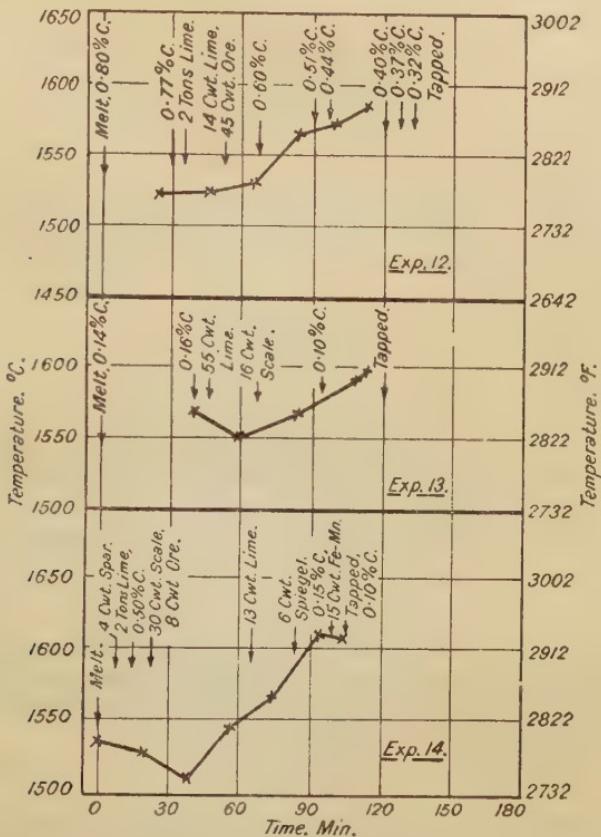


FIG. 2B (see Fig. 2A).—Temperature Variations during the Refining Process due to Bath Additions.

would be influenced by the prevailing temperature of the bath at this stage, *i.e.*, the greater the difference in metal and gas temperatures, the steeper the gradient between the slag and metal. Test 19, with the lowest metal temperature at the going-on or tapping period, shows the greatest variation,  $47^{\circ}$  C. ( $84^{\circ}$  F.), whilst in No. 16, with the highest temperature, the slag was only  $1^{\circ}$  C. ( $2^{\circ}$  F.) hotter than the metal. Assuming 6 in. of slag in the case of No. 19 and a temperature gradient of  $9^{\circ}$  C. ( $16^{\circ}$  F.) per foot in the metal, this gives a rough approximation of over  $100^{\circ}$  C. ( $180^{\circ}$  F.) per foot of slag.

TABLE IV.—*Relative Metal and Slag Temperatures.*

No.	Bath Condition.	Carbon, %.	Metal Temp.	Slag Temp.	Difference.	Remarks.
			° C.	° F.	° C.	° F.
15A	Melted	0.86	1587	2834	1564	2848
15B	22 min. after feed of $2\frac{1}{2}$ tons of mill scale	0.65	1550	2822	1554	2829
15C	30 min. after 15B	0.54	1580	2876	1580	2876
16	Going-on	0.18	1637	2980	1638	2982
17	Going-on	0.30	1606	2922	1613	2936
18	Tapping	0.10	1590	2894	1627	2960
19	Going-on	0.68	1571	2860	1618	2944
20A	Going-on	0.14	1579	2874	1613	2936
20B	Tapping	0.10	1600	2912	1631	2968
21	Going-on	0.31	1605	2920	1631	2968

The physical and chemical properties of the slag would have an influence upon the deviation of the slag and metal temperatures. An indication is given of the low thermal conductivity of molten slag as compared with steel by the steep temperature gradients which can be set up through slags averaging 5 in. in thickness.

### Summary.

A quick-immersion temperature reading made at the centre of the basic open-hearth bath at 9 in. depth can be taken as representative of the mean temperature within  $\pm 5.5^\circ$  C. ( $9.9^\circ$  F.).

When the bath is on the boil the temperature distribution in both vertical and horizontal planes falls within relatively narrow limits.

The vertical temperature gradient in furnaces of this type would probably average  $10^\circ$  C. ( $18^\circ$  F.) per foot under normal conditions.

In the horizontal plane the bath is slightly hotter under the gas than at the outlet end and tends to be hotter near the front bank than on the longitudinal centre-line.

The uniformity of temperature in the bath is governed by its activity.

With regard to the accuracy of the results of steel temperature measurements, the mean deviation from the standard position is of the same order as the probable instrumental errors. The measured temperature would therefore be accurate to within  $\pm 10^\circ$  C. ( $18^\circ$  F.) if both of these factors operated in the same direction. In most normal cases the accuracy would probably be  $\pm 5^\circ$  C. ( $9^\circ$  F.).

During refining a superheat of approximately  $40^\circ$  C. ( $72^\circ$  F.) prevails at the beginning of the reaction period, rising to  $70$ – $100^\circ$  C. ( $126$ – $180^\circ$  F.) at the going-on stage.

Bath additions of lime, scale or ore cause only a very temporary depression of temperature.

With furnaces of this type and size there is a reduction of temperature of about  $1^\circ$  C. ( $2^\circ$  F.) per min. when the gas is off.

Slag temperatures were higher by from 1° C. (2° F.) to 47° C. (84° F.) than the steel temperatures, depending upon the state of the bath and the prevailing steel temperature. The lower the metal temperature of a bath at the going-on or tapping stages, the greater was the difference between the slag and metal temperatures. Activity of the bath equalised the slag temperatures as well as those of the steel.

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# BARRIER-LAYER PHOTO-ELECTRIC CELLS FOR TEMPERATURE MEASUREMENT.\*

BY T. LAND, M.A. (RESEARCH DEPARTMENT, MESSRS. WILLIAM JESSOP & SONS, LTD., SHEFFIELD).

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## SUMMARY.

The selenium barrier-layer photo-electric cell offers many advantages for the measurement of temperatures in the foundry. Such cells have previously been used for temperature measurement, but little has been known about their limitations or their calibration. Ten cells were investigated and their fatigue, their temperature coefficients and their departure from linear response were determined. The calibration of each cell was established, using a black-body furnace and a tungsten-ribbon-filament lamp as sources of radiation. The theoretical investigation shows the relation of the calibration to the spectral sensitivity and the correction which must be applied when a tungsten lamp is used as a temperature standard. It was established that if allowance was made for the small differences in sensitivity between individual cells (about  $\pm 4\%$ ), a single table adequately represented the calibration of the cells. Nine of the ten cells proved satisfactory for temperature measurement. The design of the optical system and its effect on the calibration of the pyrometer were studied theoretically and experimentally, and a basis for the design and calibration of pyrometers was laid down.

## INTRODUCTION.

IN steelmaking the measurement and control of high temperatures is a matter of considerable practical importance, and notable advances in the technique of measurement have been made in recent years. The measurement of liquid steel temperatures in the melting furnace has received particular attention, and a satisfactory solution of the problem has been reached. The measurement of the temperature of the liquid steel in the foundry is at a less advanced stage of development, and it was considered that the barrier-layer photo-electric cell might provide a useful means of measuring such temperatures under foundry conditions.

The measurement of temperatures in the foundry has usually been carried out with disappearing-filament optical pyrometers. These have given good service, but are not beyond criticism. The chief alternative would be the total-radiation pyrometer, but this also has its limitations under foundry conditions. Without detail-

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ing the virtues or vices of each, it can be stated that an instrument combining the sensitivity of the optical pyrometer with the direct reading given by the total-radiation pyrometer would be most welcome. The photo-electric cell offers this combination, and has the additional merit of very rapid response. Cells of British manufacture are now available which are claimed to be superior in sensitivity and stability to any previously manufactured commercially, and preliminary tests showed that the cells were very reliable. An investigation has, therefore, been made of the suitability of this type of cell for temperature measurement.

#### *Photo-electric Cells.*

For those who are not familiar with photo-electric cells it may be helpful to explain that these are of two distinct types. The vacuum and gas-filled cells are in appearance not unlike a radio valve and operate on the principle of the photo-electric emission from surfaces sensitised by caesium, potassium or other photo-sensitive elements. The current from such a cell is very small, and must be amplified before it can be used to operate an indicator or recorder; furthermore, the cell requires an external source of potential for its operation, and the current obtained depends, in some cases rather critically, upon the voltage applied.

The barrier-layer type of cell, with which we are at present concerned, is of totally different construction and is probably most widely known from its use in photographic exposure meters. It consists of a small disc, usually of iron, upon which is laid a thin layer of selenium, which is further covered by a transparent metallic film. The cells used in the present investigation were about the size of a halfpenny. The barrier-layer cell generates its own current, requiring no externally applied voltage, and a current large enough to operate an indicator or recorder can readily be obtained. Selenium barrier-layer cells have in the past shown certain unfortunate features which have made the more careful investigators rightly cautious in using them for precision measurements. The cells tested in the present series of experiments proved adequately reliable for the purpose in view.

#### *Previous Work.*

The use of photo-electric cells for temperature measurement is not new. Certain British companies have, for some time, marketed pyrometers employing vacuum photo-electric cells. Barrier-layer cells have been used experimentally by Schofield in his work on liquid steel temperature measurement, and for the same purpose such cells have been used in America in the Oseland Tube method.<sup>(1)</sup> Larsen and Shenk<sup>(2)</sup> have described a pyrometer employing a barrier-layer cell, which they used to measure the temperature of an open-hearth furnace roof, and other industrial applications of photo-

electric pyrometers have been described by Sosman.<sup>(3)</sup> Dobbins, Gee and Rees<sup>(4)</sup> used a simple photo-electric pyrometer to detect change points in high-temperature heating curves in their work on refractory materials. Photo-electric colour pyrometers have been described by Russell, Lucks and Turnbull,<sup>(5)</sup> by Lindemann and Keeley<sup>(6)</sup> and by Hubing,<sup>(7)</sup> whilst the allied problem of photo-electric colour matching has been discussed by Campbell and Gardiner.<sup>(8)</sup>

Although photo-electric cells have been used by several workers for temperature measurement, the calibration appears to have been more or less empirical. Usually the cell current has been compared with readings taken with an optical pyrometer and the logarithm of the cell current plotted against the logarithm of the absolute temperature. In this way different observers have concluded that the cell current varies as the twelfth or thirteenth power of the absolute temperature. Only in the case of the colour pyrometer<sup>(5)</sup> has the calibration been given a theoretical foundation, and there is little reference to the dimensions of the optical systems. Furthermore, few or no quantitative data have been published on the errors which may arise from different sources.

#### *Scope of the Investigation.*

The disappearing-filament pyrometer can be calibrated by reference to the laws of radiation. It is shown in Part I. that the photo-electric cell can be calibrated in a similar way. It is only necessary to know the spectral distribution of sensitivity of the cell and its deviation from linear response to illumination intensity in order to calculate the ratio of the currents generated when the pyrometer is sighted on objects at different temperatures. A black-body furnace is not a very convenient source of radiation, and it is shown that a tungsten-ribbon-filament lamp can be used as a secondary standard of temperature for the calibration of cells. The optical system of the pyrometer is discussed, and the effect of varying the different dimensions of the system is outlined.

Part II. of the paper is an account of the experimental work done on the general properties and the calibration of the photo-electric cells. For normal industrial practice, an accuracy of  $\pm 5^\circ \text{ C.}$  ( $\pm 9^\circ \text{ F.}$ ) is adequate, and there are many cases in which an uncertainty of  $\pm 10^\circ \text{ C.}$  ( $\pm 18^\circ \text{ F.}$ ) is not serious. With this consideration in mind, no attempt has been made to calibrate the cells to an accuracy of better than  $\pm 3^\circ \text{ C.}$  ( $\pm 5^\circ \text{ F.}$ ). To obtain a further degree of precision would entail a great elaboration of the experimental technique, which was not thought to be necessary. It has, however, been possible to provide a standard of illumination of high precision, and measurements of the fatigue and other general properties of the cells have been made to an accuracy of about one part in a thousand.

The results of the calibration are given in the form of Tables

in Appendix I. Appendix II. comprises the details of some of the experimental results.

### PART I.—THEORY OF THE PHOTO-ELECTRIC PYROMETER.

#### *Notation.*

The following symbols are used throughout this paper :

- $i$  = cell current.
- $i_o$  = constant dependent on the dimensions of the optical system and on the sensitivity of the photo-electric cell.
- $y$  =  $\log_{10} i$ .
- $T$  = true temperature of source ( $^{\circ}$  K.).
- $T_p$  = brightness temperature ( $^{\circ}$  K.) as measured by photo-electric pyrometer.
- $T_o$  = brightness temperature ( $^{\circ}$  K.) as measured by optical pyrometer.
- $x = \frac{10^4}{T_p}$ .
- $\lambda$  = wave-length of radiation.
- $\lambda_p$  = effective wave-length of photo-electric pyrometer.
- $\lambda_o$  = effective wave-length of optical pyrometer.
- $\mu$  = micron ( $10^{-4}$  cm.).
- $J_{\lambda} d\lambda$  = energy radiated by black body in wave-length range  $\lambda$  to  $\lambda + d\lambda$ .
- $C_1, C_2$  = Wien's radiation constants ( $C_2 = 1.432$  cm.  $^{\circ}$  K.).
- $S_{\lambda}$  = spectral sensitivity of cell.
- $\tau_{\lambda}$  = spectral transmission of filter and lens system.
- $\tau_m$  = mean transmission of lens system.
- $V_{\lambda}$  = visibility function of the eye.
- $E_{\lambda}$  = spectral emissivity of tungsten.
- $E_p$  = effective emissivity of lamp for photo-electric pyrometer.
- $E_o$  = effective emissivity of lamp for optical pyrometer.
- $E_m$  = mean emissivity of tungsten for both pyrometers.
- $\tau'_{\lambda}$  = spectral transmission of glass envelope of lamp.
- $\tau'_m$  = mean transmission of glass envelope.
- $b$  = a constant affecting the departure from linear response of the photo-electric cell, defined in equation (5).
- $L$  = intrinsic luminosity of the hot surface.
- $I$  = intensity of illumination of the cell.
- $A_l$  = area of lens stop.
- $A_e$  = area of cell stop.
- $s = \frac{A_l A_e}{d^2}$ , called the "size factor" of the pyrometer.
- $d$  = distance between stops.
- $i_s$  = cell current when stops are of unit area and unit distance apart.
- $c$  = cell constant.

#### *Theory of Calibration.*

The theory of the photo-electric pyrometer is similar to that of the disappearing-filament pyrometer, and is based on Wien's formula for black-body radiation :

$$J_{\lambda} = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}}$$

The photo-electric cell is only sensitive to a range of wave-lengths roughly the same as the visible spectrum. If the cell were only

sensitive to a very narrow band of wave-length  $\lambda$  the cell current would be given by :

$$i = i_0 \lambda^{-5} e^{-\frac{C_2}{\lambda T}}.$$

If the spectral sensitivity of the cell at wave-length  $\lambda$  is  $S_\lambda$  the cell current is :

$$i = i_0 \int_0^\infty S_\lambda J_\lambda d\lambda.$$

If a lens and filter of transmission  $\tau_\lambda$  are included in the optical system :

$$i = i_0 \int_0^\infty \tau_\lambda S_\lambda J_\lambda d\lambda \quad . . . . . \quad (1)$$

Since the cell is sensitive only to a relatively narrow band of wavelengths we may say that the pyrometer has a "mean effective wave-length"  $\lambda_p$  over the temperature range  $T_1$  to  $T_2$  defined by the relation :

$$\frac{i_1}{i_2} = \frac{J_\lambda(\lambda_p, T_1)}{J_\lambda(\lambda_p, T_2)} = \frac{\int_0^\infty \tau_\lambda S_\lambda J_\lambda(T_1) d\lambda}{\int_0^\infty \tau_\lambda S_\lambda J_\lambda(T_2) d\lambda} \quad . . . . . \quad (2)$$

This definition of the mean effective wave-length is exactly comparable with the definition used for the disappearing-filament pyrometer :

$$\frac{J_\lambda(\lambda_o, T_1)}{J_\lambda(\lambda_o, T_2)} = \frac{\int_0^\infty \tau_\lambda V_\lambda J_\lambda(T_1) d\lambda}{\int_0^\infty \tau_\lambda V_\lambda J_\lambda(T_2) d\lambda}.$$

The visibility function of the eye,  $V_\lambda$ , takes the place of the spectral sensitivity of the photo-electric cell.

From equation (2) we may write :

$$\frac{i_1}{i_2} = \frac{J_\lambda(\lambda_p, T_1)}{J_\lambda(\lambda_p, T_2)} = \frac{e^{-\frac{C_2}{\lambda_p T_1}}}{e^{-\frac{C_2}{\lambda_p T_2}}}.$$

$$\therefore \log_e \frac{i_1}{i_2} = -\frac{C_2}{\lambda_p} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad . . . . . \quad (3)$$

Writing :

$$x = \frac{10^4}{T} \quad (T_p = T \text{ for black body}),$$

$$y = \log_{10} i,$$

$$y_1 - y_2 = -\frac{C_2}{\lambda_p} (x_1 - x_2) \log_{10} e,$$

$\lambda_p$  will now be measured in microns.

In the limit, as  $T_2 \rightarrow T_1$ :

$$\frac{dy}{dx} = -\frac{C_2}{\lambda_p} \cdot \log_{10} e \quad \dots \dots \dots \quad (4)$$

$\lambda_p$  is now the effective wave-length at temperature  $T$ .

The cell current has been assumed to be proportional to the intensity of illumination, and this is not strictly true for a barrier-layer cell. The deviation from linear response is small, and it will be seen when the experimental results are considered that the relation between illumination ( $I$ ) and current may usually be expressed in the form :

$$\log i = a + b \log I \quad \dots \dots \dots \quad (5)$$

$b$  frequently has a value of about 0.99. The equation to the calibration curve is therefore :

$$\frac{dy}{dx} = -\frac{bC_2}{\lambda_p} \cdot \log_{10} e \quad \dots \dots \dots \quad (6)$$

It is found that when the logarithm of the cell current is plotted against the reciprocal of the absolute temperature, a line is obtained which is very nearly straight. It will be noticed that the slope of the line is a measure of the effective wave-length of the cell, and the slight curvature of the calibration line is an indication of the small variation of the effective wave-length with the temperature of the source.

This method of presenting the calibration of the pyrometer is clearly much more logical and informative than the usual method of plotting the logarithm of the cell current against the logarithm of the absolute temperature.

It is interesting to note that the theory outlined above is similar to that derived by Pirani and Miethling<sup>(9)</sup> for the relation between the brightness of a black body and its temperature. Using the experimental results of Nernst<sup>(10)</sup> and of Lummer and Pringsheim,<sup>(11)</sup> they found a linear relationship between the logarithm of the brightness and the reciprocal of the absolute temperature, and the value of the effective wave-length calculated from the slope of the line was shown to agree with a value obtained directly by Ives.<sup>(12)</sup>

#### *Tungsten Lamp as a Secondary Standard.*

The tungsten-ribbon-filament lamp has proved a valuable secondary standard of brightness temperature for the calibration of disappearing-filament optical pyrometers. It is similarly useful for calibrating photo-electric pyrometers. Since the true temperature of the lamp is considerably higher than its brightness temperature (the emissivity at 0.66  $\mu$  is approximately 0.44), the brightness temperature will depend on the effective wave-length of the pyrometer. For this reason a correction is necessary when a lamp calibrated by an optical pyrometer is used to calibrate a photo-electric pyrometer.

A tungsten filament is not a perfectly grey body, so for exact calculations the spectral emissivity  $E_\lambda$  of the filament would have to be measured, and also the transmission  $\tau'_\lambda$  of the glass envelope of the lamp. The effective emissivities  $E_o$  and  $E_p$  for the optical and photo-electric pyrometers would be given by :

$$E_o = \frac{\int_0^\infty E_\lambda \tau'_\lambda \tau_\lambda V_\lambda J_\lambda d\lambda}{\int_0^\infty \tau_\lambda V_\lambda J_\lambda d\lambda} .$$

$$E_p = \frac{\int_0^\infty E_\lambda \tau'_\lambda \tau_\lambda S_\lambda J_\lambda d\lambda}{\int_0^\infty \tau_\lambda S_\lambda J_\lambda d\lambda} .$$

If the true temperature of the filament is  $T$  and the brightness temperatures measured by optical and photo-electric pyrometers are  $T_o$  and  $T_p$ , respectively :

$$E_o J_\lambda(\lambda_o, T) = J_\lambda(\lambda_o, T_o).$$

$$\therefore E_o \lambda_o^{-5} e^{-\frac{C_2}{\lambda_o T}} = \lambda_o^{-5} e^{-\frac{C_2}{\lambda_o T_o}}.$$

$$\therefore \log_e E_o = \frac{C_2}{\lambda_o} \left( \frac{1}{T} - \frac{1}{T_o} \right) . . . . . \quad (7)$$

Similarly :

$$\log_e E_p = \frac{C_2}{\lambda_p} \left( \frac{1}{T} - \frac{1}{T_p} \right) . . . . . \quad (8)$$

$$\therefore \frac{1}{T_o} - \frac{1}{T_p} = \frac{1}{C_2} \{ \lambda_p \log_e E_p - \lambda_o \log_e E_o \} . . . \quad (9)$$

If we assume tungsten to be a grey body of emissivity  $E_m$  and the glass envelope to transmit uniformly a proportion  $\tau'_m$  of the light in all parts of the spectrum, i.e. :

$$E_p = E_o = \tau'_m E_m,$$

then :

$$\frac{1}{T_o} - \frac{1}{T_p} = \frac{\lambda_p - \lambda_o}{C_2} \cdot \log_e \tau'_m E_m . . . . . \quad (10)$$

Equations (9) and (10) define the difference in brightness temperatures of a lamp as measured by the two types of pyrometer.

When a photo-electric pyrometer is sighted first on a black body at temperature  $T_o$  and then on a tungsten-strip lamp the brightness temperature of which as measured by an optical pyrometer is also  $T_o$ , the difference  $\Delta y$  in the logarithms of the cell currents is :

$$\begin{aligned} \Delta y &= \left( \frac{10^4}{T_o} - \frac{10^4}{T_p} \right) dy \\ &= \frac{\lambda_o - \lambda_p}{C_2} \cdot \log_e \tau'_m E_m \cdot \frac{b C_2}{\lambda_p} \cdot \log_{10} e, \\ &= \frac{\lambda_o - \lambda_p}{\lambda_p} \cdot b \log_{10} \tau'_m E_m . . . . . \quad (11) \end{aligned}$$

When the black-body calibration is to be derived from observations on a tungsten lamp it is necessary to know the effective wave-length of the pyrometer at each temperature, in order to evaluate the quantity  $\Delta y$  in equation (11). The effective wavelength must, however, be derived from the black-body calibration, so a method of successive approximations is necessary.

The difference between the gradients of the black-body and tungsten-lamp calibration curves is :

$$\frac{d\Delta y}{dx} = - \frac{b\lambda_o}{\lambda_p^2} \cdot \frac{d\lambda_p}{dx} \cdot \log_{10} \tau'_m E_m \quad \dots \quad (12)$$

In the first approximation we use in this equation values of  $\lambda_p$  and  $d\lambda_p/dx$  derived from the slope of the tungsten-lamp calibration curve. The slope of the black-body curve is then obtained from the slope of the tungsten-lamp curve by subtracting  $d\Delta y/dx$ , and hence the first approximation to the effective wave-length at each temperature is obtained from equation (6). A second approximation using the first approximation to  $\lambda_p$  in equation (12) usually gives identical values of  $\lambda_p$ , so the process is not unduly laborious. The final step of calculating  $\Delta y$  and hence the black-body calibration can then be completed.

In calculating the values given in Table VIII. the foregoing procedure was used, assuming values of 0.44 and 0.90 for  $E_m$  and  $\tau'_m$ , respectively, and 0.99 for  $b$ .

#### *Geometry of the Optical System.*

A simple optical system was used for the experiments. This consisted of a single lens (double-convex) and two apertures, one placed in contact with the lens between it and the cell, and the other placed in front of the cell.

Suppose that an image of a hot body at  $O$  (Fig. 1) is formed at  $I$ , and that a quantity of light  $L$  is emitted per unit solid angle

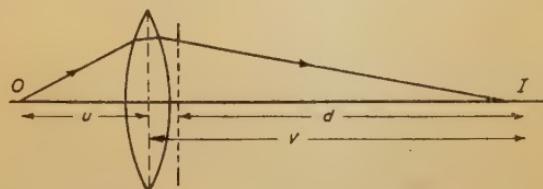


FIG. 1.—Simple Optical System (diagrammatic)

from each square centimetre of the object (*i.e.*,  $L$  is the "intrinsic luminosity" of the object). Suppose that an aperture of area  $A_l$  is placed near the lens, between the lens and the photo-electric cell. Let the image  $I$  be formed on an aperture of area  $A_c$  in front of the cell. Let the distance between the lens aperture and the cell aperture be  $d$ . Referring to Fig. 1 it will be seen

that the lens stop has the same effect as an aperture of area  $A_l \times (v^2/d^2)$  placed at the optical centre of the lens. The solid angle of useful light coming from any point on the object is therefore  $(A_l/u^2) \times (v^2/d^2)$ . The area of the object producing an image of area  $A_c$  is  $A_c \times (u^2/v^2)$ . Hence, the light reaching the cell is equal to :

$$\tau_m \times L \times \frac{A_c A_l}{u^2} \times \frac{v^2}{d^2} \times \frac{u^2}{v^2} = \frac{A_c A_l}{d^2} \times L \tau_m.$$

The factor  $A_c A_l / d^2$  will be called the "size factor" of the pyrometer, and will be denoted by the symbol  $s$ . Provided that the photo-electric cell is uniformly sensitive over its whole area we may write :

$$i = s \cdot i_s,$$

where  $i_s$  is a standard current, characteristic of the cell and the temperature of the hot object.

It will be shown later that the currents for different cells vary by a factor typical of each cell, and very nearly independent of the temperature of the source. We may therefore write :

$$i = sci_s,$$

in which  $c$  is called the cell constant.

## PART II.—EXPERIMENTAL WORK.

### *Method.*

The experimental investigation covered a total of ten cells,\* each 25 mm. in dia., which were obtained in three batches :

- (i) Cell *A*.
- (ii) Cells *B*, *C* and *D*.
- (iii) Six "matched" cells designated *G*, *H*, *J*, *K*, *L* and *M*.

The photo-cell current was measured with the Campbell-Freeth<sup>(13)</sup> circuit shown in Fig. 2. The photo-electric cell *C* generates a current which passes through the resistance  $R_2$  and the galvanometer *G*. The cell current passing through *G* is balanced by an equal and opposite current derived from the vernier potentiometer *P* and passing through the 10,000-ohm resistance  $R_1$ . The method of measurement is to adjust the potentiometer until the galvanometer returns to its zero position. There is then no potential difference across the galvanometer, and the cell current is equal to the potentiometer reading divided by the resistance  $R_1$ . The correction necessary for the resistance of the potentiometer was rarely more than one part in 1000. The sensitivity of the galvanometer was approximately 1500 mm. per micro-amp. In all measure-

\* The cells were manufactured by Messrs. Evans Electro-selenium, Ltd.

ments of cell current the "dark cell current" obtained when the direct illumination from the hot source was interrupted was also measured. In this way allowance could be made for stray illumination reaching the cell. In almost all cases the dark cell current

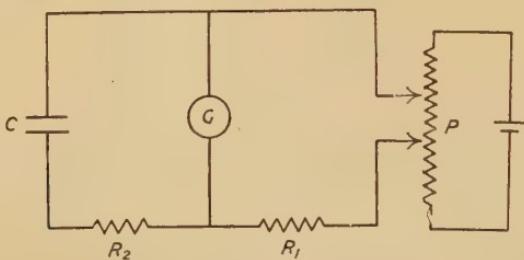


FIG. 2.—Measuring Circuit.

was less than 1% of the current from the illuminated cell, and in most cases very much less than 1%. In all calibration measurements the optical system consisted of a single lens and two stops, as mentioned above. The majority of observations were taken with a lens of 5 cm. focal length and an aperture 1 cm. in dia.

#### *Sources of Radiation.*

The black-body furnace consisted of a Pythagoras tube, 12 in. long, wound with platinum tape and suitably insulated. The temperature was measured at the centre of the furnace with a new platinum/13%-rhodium-platinum thermocouple and a vernier potentiometer. The internal diameter of the furnace tube was 10 mm., and a twin-bore refractory rod, 8 mm. in dia., was used to insulate the thermocouple over the 2 cm. nearest to the thermojunction. The next twin-bore insulator behind was arranged to have its holes out of alignment with this end insulator, so that the two holes carrying the thermocouple wire formed a small black body. It was assumed that black-body conditions had been obtained when the two holes entirely disappeared from the field of view. A silica tube, 2 cm. long, was inserted from the open end of the furnace in contact with the end of the twin-bore rod, to reduce any selective reflection of radiation from local hot parts of the furnace tube. The optical system was carefully aligned with the furnace tube to ensure that the full radiation reached the photo-electric cell. The furnace was heated by alternating current, and it was found that there was no significant leakage of current from the furnace winding to the thermocouple.

The majority of observations were made with two tungsten-ribbon-filament gas-filled lamps, which had been calibrated at the National Physical Laboratory some months previously. It was found that lamp 76 gave a cell current about 5% greater than lamp 85 when both were adjusted to the same temperature. This corre-

sponds to a difference of about  $5^{\circ}$  at  $1350^{\circ}$  C. ( $9^{\circ}$  at  $2460^{\circ}$  F.), and about  $7^{\circ}$  at  $1700^{\circ}$  C. ( $12^{\circ}$  at  $3090^{\circ}$  F.). This difference is within the uncertainty of calibration quoted by the National Physical Laboratory. Lamp 85 was recalibrated by the National Physical Laboratory during the experiments, and the new calibration agreed quite well with the average value of the previous calibrations of the two lamps. All observations quoted in the paper were made with lamp 85 and the new calibration.

The lamp current was provided by four 12-V. batteries, and regulated through a resistance board in which the only sliding contact was arranged to carry only a small proportion of the total current. At the time the batteries were in poor condition, and in the later part of the investigation they were simultaneously recharged from the D.C. main. For the most accurate work a Tinsley D.C. amplifier was modified to provide a controller which kept the lamp current constant to within better than one part in 10,000. The lamp current was passed through a standard 4-point,  $\frac{1}{10}$ -ohm resistor, and the potential across the terminals was measured on a vernier potentiometer.

### *Experimental Results.*

The following properties of the ten cells were investigated :

- (1) Fatigue.
- (2) The relation between illumination and current.
- (3) The temperature coefficient.
- (4) Calibration against the temperature of the source.

These properties are affected to a greater or less degree by the following factors :

- (1) The temperature of the cell and its recent temperature history.
- (2) The intensity of illumination.
- (3) The conditions of illumination over a period of several hours before the experiment.
- (4) The area of cell exposed.
- (5) The resistance of the measuring circuit.

To investigate the interrelation of all these factors in their effect on the different properties of the ten cells would have been most laborious. It was clearly necessary to limit the extent of the survey. The experiments were therefore confined to conditions likely to be experienced in practice when the cells are used for temperature measurement. The temperature of the cell was kept in the region of  $18\text{--}25^{\circ}$  C. ( $65\text{--}77^{\circ}$  F.); the area of the cell exposed was usually 1 sq. cm. and the resistance of the measuring circuit zero. In this way the scope of the work was kept within reasonable bounds.

*Temperature Coefficient of Lamp.*

The temperature of the lamp filament for a given current is affected by the temperature of the air surrounding the lamp. It was clear from the initial experiments that the change was very small, but it was thought advisable to measure the magnitude of the effect. The lamp was enclosed in a cylinder of Uralite, 5 in. in dia., in which a suitable hole was provided for the lens of the optical system. The air temperature was measured by a mercury thermometer fixed vertically  $\frac{5}{8}$  in. from the surface of the lamp bulb. The cell was thermostatically controlled and was first illuminated for several hours to avoid fatigue effects, the lamp cover being removed. The Uralite cover was then placed over the lamp and the air temperature was allowed to rise under the heating effect of the lamp. In this way a change in air temperature was obtained without disturbing the still air. Any air circulation, even with warm air blown into the enclosure, seriously reduced the filament temperature. The temperature coefficients measured were very small and barely outside the experimental error, as shown in Table I. The coefficient is the percentage change in the illumination of the cell for each  $1^{\circ}$  C. change of air temperature.

TABLE I.—*Lamp Temperature Coefficients.*

Lamp Temperature. ° C.	Range of Air Temperatures. ° C.	Temperature Coefficient of Lamp. % per ° C.
1750	30-45	{ 0.03 0.04
1550	30-45	0.02
1350	26-36	0.07

The lamp coefficient is so small that it would rarely affect results by more than one or two parts per 1000. It was found advisable for accurate work to keep the cover over the lamp to protect it from draughts, which do have an appreciable effect.

*Fatigue.*

When a cell is illuminated it does not immediately give a steady current. The current is initially, perhaps, 5% above its final steady value, and falls at first rapidly and then increasingly slowly until it reaches a sensibly steady value. This effect has been called "fatigue" or "drift." The amount and rapidity of the drift depend on the illumination of the cell during the previous few hours.

During the experiments it was noticed that a "reverse fatigue" or recovery occurred when a cell, after being brightly illuminated, was illuminated at, say, a tenth of the previous intensity. The magnitude and speed of the effect was of the same order as the

normal fatigue. It would therefore appear that the sensitivity of the cell is a function of the intensity of illumination. The change of sensitivity with illumination is sluggish and takes several hours to complete.

In the practical application of the cells it is intended to use

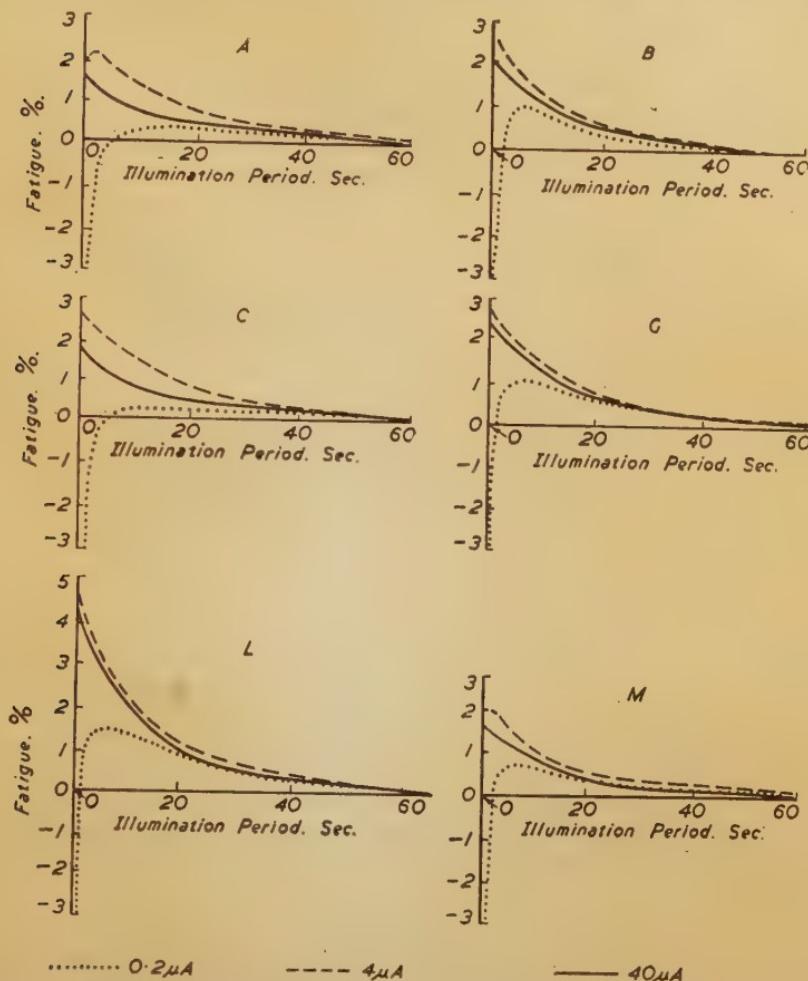


FIG. 3.—Fatigue during First Minute after Illumination. Cell aperture 1 sq. cm. Darkened for 5 min. Measuring circuit resistance zero.

them in two ways. They will be employed in continuous recording over long periods and also for rapid measurements for intervals of from 1 to 10 sec. The fatigue during the first minute was measured with a special Tinsley amplifier and recorder, which gave a full-scale deflection on 0.2 micro-amp. in  $\frac{1}{2}$  sec. when adjusted to its

maximum sensitivity. The fatigue over long periods was measured on a vernier potentiometer.

The results of the short-period tests are shown in Fig. 3. Three intensities of illumination were used, giving 0.2 micro-amp., 4 micro-amp. and 40 micro-amp., respectively, on an area of 1 sq. cm., the cell being darkened for 5 min. before the observations. The curves for the higher illuminations are almost identical, but for 0.2 micro-amp. the current reaches its maximum value only after about 5 sec. This is because the cell acts as an imperfect condenser, and with low illuminations an appreciable time is required for it to become charged. It is noticeable that for each cell a current of 4 micro-amp. gives a slightly higher fatigue than 40 micro-amp.,

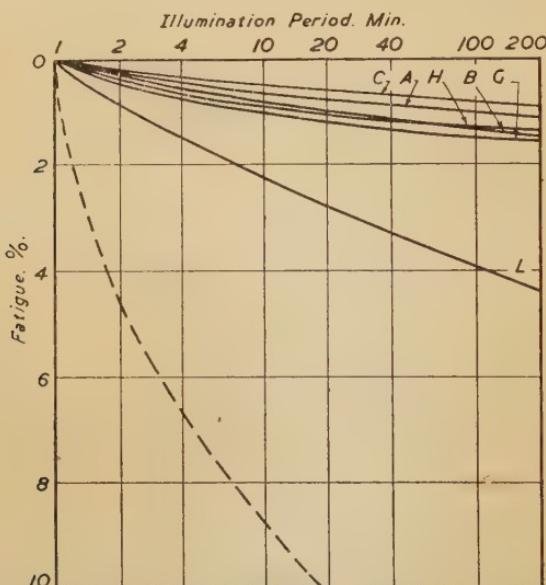


FIG. 4.—Fatigue from First Minute after Illumination. Cell aperture 1 sq. cm. Current 10 micro-amp. Darkened for 30 min. Measuring circuit resistance zero.

but the difference is barely outside the experimental error. It appears that the fatigue is not greatly affected by the intensity of illumination. The curves show that the fatigue during the first minute was between  $1\frac{1}{2}\%$  and 3% for all but one of the cells tested. Cell *L* had an abnormally high fatigue of nearly 5% in the first minute.

The long-period fatigue was measured after keeping the cell dark for 30 min. The results are shown in Fig. 4, in which the time is plotted on a logarithmic scale. Measurements were commenced one minute after illumination and continued for between 3 and 4 hr. The temperature of the cell was kept constant within

about  $\pm 0.3^\circ$  C. ( $\pm 0.6^\circ$  F.). The dotted line shows the fatigue of an older cell of a different make. The improved stability obtained in the new cells is clearly apparent.

The total fatigue after the first minute is 1- $1\frac{1}{2}$ % during the first 200 min. for all except one cell, *L*, which again has abnormal fatigue properties. This cell is also of lower sensitivity than the other cells tested, and is assumed to be defective.

The effect of darkening the cell for different periods was next investigated. Fig. 5 is a composite picture summarising the results

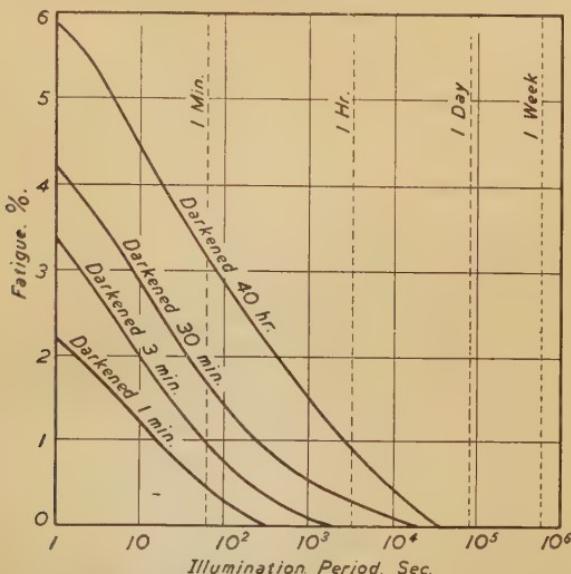


FIG. 5.—Fatigue after Different Periods of Darkening.

of several experiments. The effect of darkening for a certain length of time is only apparent for a similar period after the cell is illuminated. The fatigue then decreases and the cell returns to its previous tendency. The curves are therefore continued only to a certain point, beyond which the previous history of the cell becomes the dominant factor. The maximum fatigue was measured after 40 hr. darkening and totalled about 6%, more than half of which occurred during the first minute. The initial shape of the fatigue curve does not seem to vary greatly with the period of darkening. Fig. 6 records the results of an experiment undertaken to see if the cell returned to the same reading after different periods of illumination and darkening. After illuminating the cell for  $\frac{1}{2}$  hr. it was darkened for a similar period before commencing the first set of observations (curve *a*). After 200 min. illumination the cell was darkened for 40 hr. and illuminated again, giving a second fatigue curve, *b*. It was then darkened again for 30 min., after which a

third fatigue curve was taken, *c*. The two fatigue curves taken after 30 min. darkening are almost exactly parallel over most of their length. The cell in each case returned to within 0·2% of the same value after 200 min. illumination.

To test the constancy of the cell current over longer periods a cell was illuminated for 6 days and the cell current was measured three times a day. The cell was thermostatically controlled at

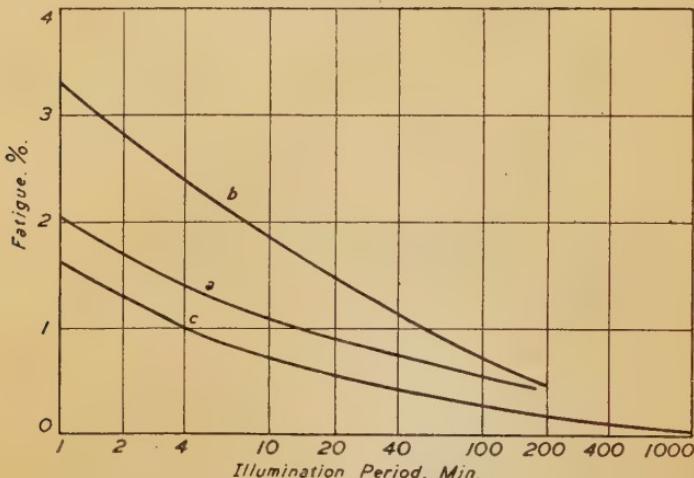


FIG. 6.—Fatigue during Successive Periods of Illumination. Cell darkened 40 hr. between (a) and (b), and 30 min. between (b) and (c).

35° C. (95° F.) throughout the test. After the first day all the observations fell within  $\pm 0\cdot1\%$  until the last day, when a decrease in cell current of 1% was noted. It is uncertain whether this was due to instability in the cell or to some change in the illumination such as might be caused by dirt deposited on some part of the optical system. The constancy of calibration over still longer periods may be judged from the results of two calibration tests taken at an interval of a month on nine different cells (Table II.). The relative sensitivities of the cells had changed by less than 1% during this period.

The sensitivity of the cell after 10 min. exposure changes at the rate of only 0·05% per min. This provides a useful standard time at which to calibrate the cell. Variations in its history before illumination produce changes of little more than 1% in the response after 10 min. illumination. The calibration figures given later in the paper refer to approximately this condition.

#### Current-Illumination Relation.

The current generated by a barrier-layer cell is not, in general, strictly proportional to the intensity of illumination. The departure

from proportionality depends chiefly on the resistance of the measuring circuit and the intensity of illumination.

The most direct and satisfactory method of investigation is the method of addition. The apparatus used for the purpose was similar in principle to that used by Atkinson, Palmer, Winch and Campbell.<sup>(14)</sup> The cell was illuminated by ten 3-watt lamps, the light from each passing through one of ten holes in the top of the cylindrical case enclosing the cell (Fig. 7). Each of the holes could be closed by covering it with a metal disc covered on the underside with black velvet. The cell was illuminated for about  $\frac{1}{2}$  hr. before commencing observations. After changing the illumination of the cell a period of 3–4 min. was allowed to elapse before a reading was taken. The cell was first illuminated by each lamp in turn, and then by two, three and four lamps together, and so on up to ten. The response from each individual cell was then again measured. After changing the illumination from ten lamps to one lamp a period of about 15 min. was allowed for the cell to attain a steady condition once more. The temperature of the cell was controlled to  $\pm 0.3^\circ$  C. ( $\pm 0.5^\circ$  F.) throughout the observations, and the total current through the ten lamps was controlled within one part in 10,000.

The results of such tests on five cells are shown in Fig. 8. The illumination from the coiled filament lamps varied on occasions by as much as 1% during the experiments. For this reason the results may be in error by as much as  $\frac{1}{2}\%$ . No attempt was made to reduce this error, because the uncertainty of the fatigue condition of the cell makes the significance of the results doubtful to at least this amount.

Another method of investigating the departure from proportionality is to illuminate the cell with a straight filament lamp at different distances from the cell. The illumination will then be inversely proportional to the square of the distance between the cell and the filament. Experiments on these lines were carried out on a simple optical bench, and the results are compared in Fig. 9

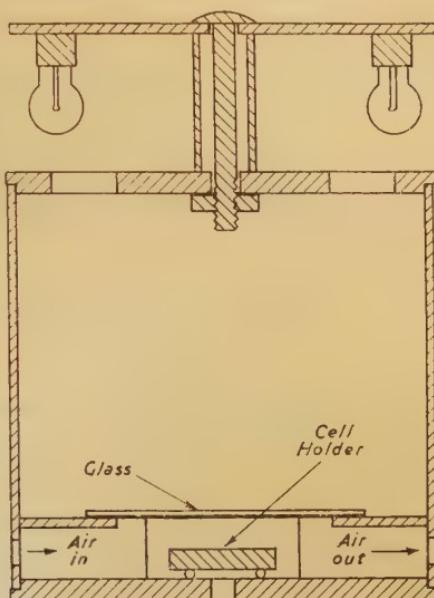


FIG. 7.—Apparatus for Measuring the Departure from Linear Response to Illumination.

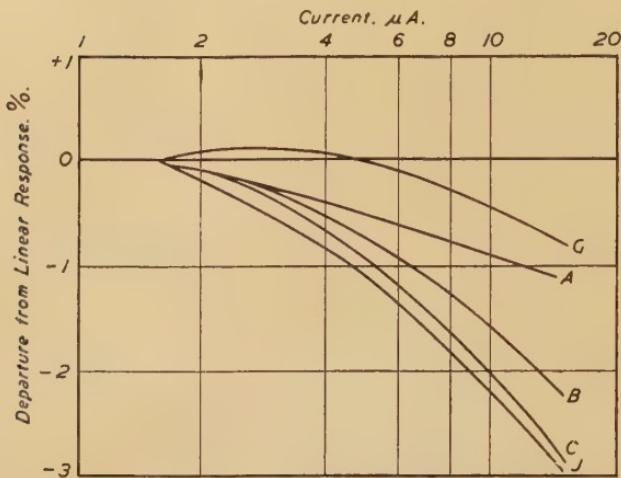


FIG. 8.—Departure from Linear Response to Illumination, by the method of addition. Cell aperture 1 sq. cm.

with those obtained by the method of addition. The agreement is as good as could be expected, considering the errors involved in the two methods and the difference of fatigue conditions. It is ideally desirable to leave the cell under each illumination intensity

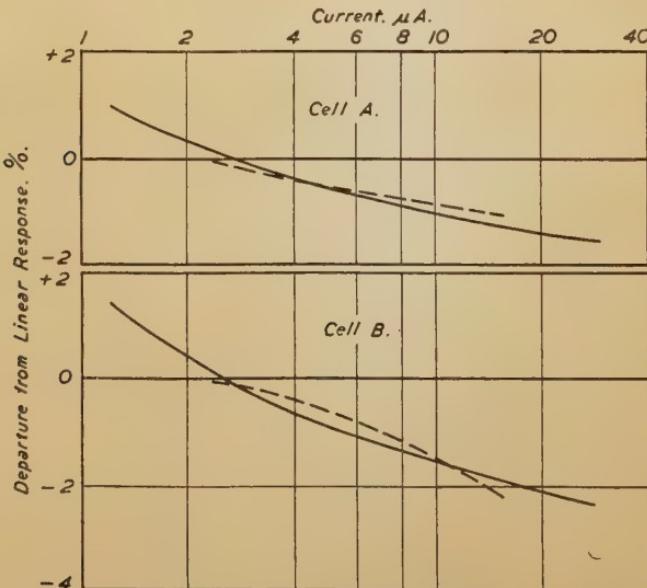


FIG. 9.—Departure from Linear Response to Illumination, by the inverse-square method (full line) and the method of addition (broken line).

for about an hour before taking an observation, but this would make the experiment impossibly protracted, and even then might not achieve the desired stability. It is therefore necessary to compromise, and the varied shapes of the curves partly reflect different fatigue conditions. It seems likely that the departure from linear response does not differ greatly from a straight line when plotted against the logarithm of the current. On increasing the current from 1.5 micro-amp. to 15 micro-amp. the departure from proportionality varies between 1% and 3% for the five cells. This corresponds to about  $1\frac{1}{2}$ ° to  $4\frac{1}{2}$ ° C. (3° to 8° F.) over a temperature interval of more than 200° C. (360° F.) at liquid steel temperatures.

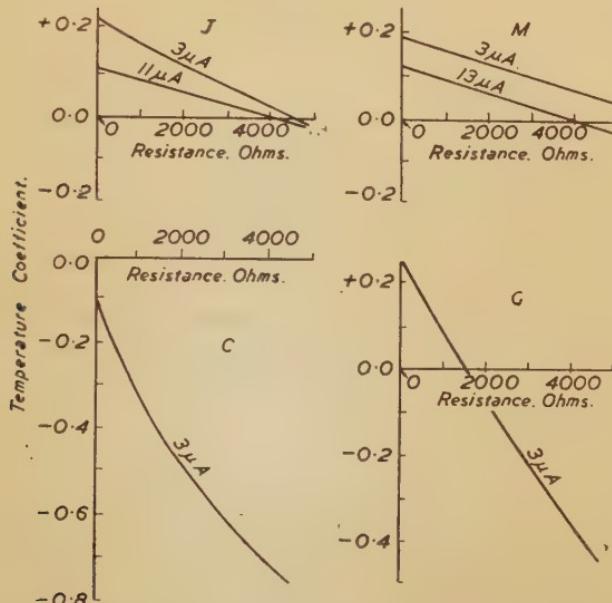


FIG. 10.—Temperature Coefficients (percentage change of cell current for 1° C.). Cell aperture 1 sq. cm.

#### *Temperature Coefficient.*

The temperature coefficient of a barrier-layer cell depends on the intensity of illumination and the resistance of the measuring circuit. The variations of the coefficients with resistance at different illuminations for four cells are shown in Fig. 10. An area of 1 sq. cm. was illuminated in this series of experiments, the temperature being 25° to 40° C. (77° to 104° F.). The effect of high illumination on an area of less than 0.2 sq. cm. is shown in Fig. 11.

The curves are all of the same type. When the measuring circuit has zero resistance the temperature coefficient lies between  $-0.1\%$  and  $+0.3\%$  per 1° C. The coefficient decreases with

increasing resistance in the measuring circuit and with increasing illumination. The effect of the resistance is much greater for some cells than for others. For most cells it is possible to choose a value

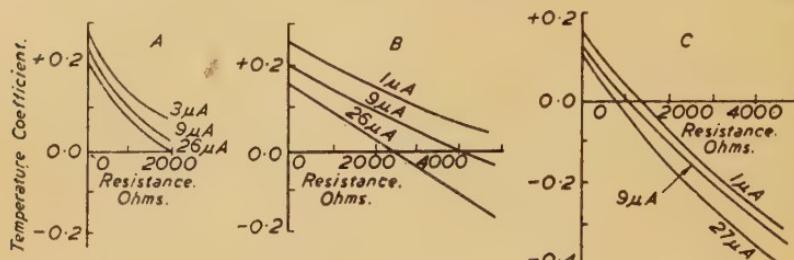


FIG. 11.—Temperature Coefficients (percentage change of cell current for  $1^{\circ}\text{C}.$ ). Cell aperture  $0.2\text{ sq. cm.}$

of the measuring circuit resistance which makes the temperature coefficient negligibly small. All these features have been noted for Weston cells,<sup>(15)</sup> and the magnitudes of the coefficients seem to be of the same order for cells from both sources.

#### *Calibration.*

The experimental results must be divided into two sections. In the earlier experiments four cells were calibrated carefully under a variety of conditions against a black-body furnace and the two standard tungsten lamps. These cells were then used for the experiments on the determination of the temperature coefficients, and were quite seriously overheated. As a result, their calibrations were somewhat changed. The later results, in which the calibrations of these cells are compared with those of the other six cells, must therefore be treated separately.

Owing to the large range of temperatures covered in the investigations and the relatively small deviations from the standard curve, it is difficult to present the results directly in graphical form. The following procedure has therefore been adopted. From all the observations two standard Tables have been drawn up. These Tables give the values of the logarithm of the "standard current"  $i_s$  (in micro-amperes) at different temperatures expressed in reciprocals of the absolute temperature. One Table is for black-body conditions and the other for a tungsten lamp calibrated at  $0.66\mu$ . The latter Table differs from the former by a factor calculated on the theory given in an earlier section of the paper. The two Tables are presented in Appendix I. (Tables VIIA. and VIIIIB.). The experimental results are, in each case, compared with these Tables, and deviations from them indicate the variations between cells and the changes which take place in any given cell.

We will first consider the calibration of the ten cells against the

tungsten-ribbon-filament lamp. Table II. shows how the cells differ in their mean sensitivity over the range 1350–1750° C. (2460–3180° F.). The calibration was repeated after an interval of 4 weeks and the agreement is remarkably good.

TABLE II.—*Difference in Sensitivity of Cells.*

Cell.	Percentage Difference from Mean.		Cell.	Percentage Difference from Mean.	
	Jan. 28, 1943.	Feb. 26, 1943.		Jan. 28, 1943.	Feb. 26, 1943.
A	+1.2	+1.7	H	+3.3	+3.8
B	-2.1	-2.4	J	-2.4	-3.1
C	-2.1	-2.1	K	-2.9	-3.1
D	+1.7	+2.1	L	...	-10.2
G	+1.9	+1.0	M	+2.1	+2.4

3180° F.). The calibration was repeated after an interval of 4 weeks and the agreement is remarkably good.

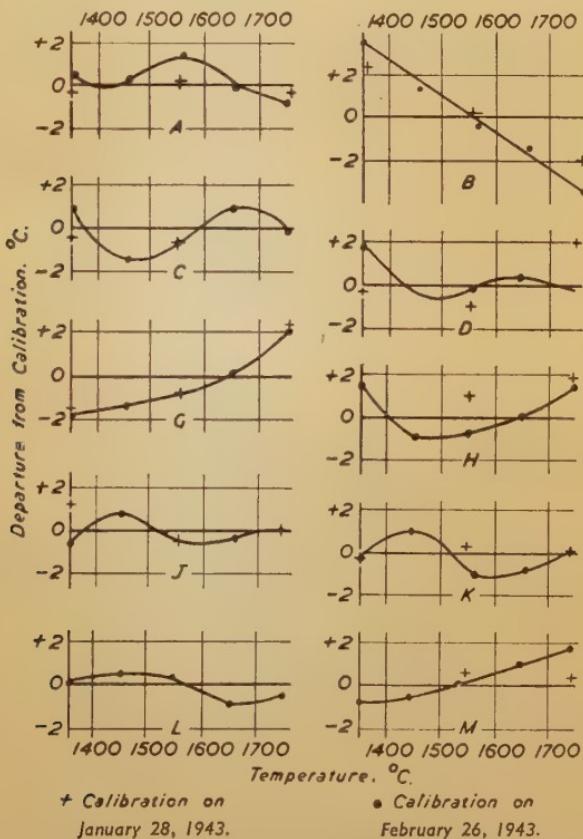


FIG. 12.—Departure of Individual Cells from Calibration given in Table VIIIIB. (Appendix I.).

The deviations of the calibration curves from the standard Table are shown in Fig. 12, in which the curves have been corrected for the variations of sensitivity shown in Table II. It will be noticed that over this large temperature range ( $400^{\circ}$  C.;  $700^{\circ}$  F.) the variation from the standard Table exceeds  $3^{\circ}$  C. ( $6^{\circ}$  F.) in only two cases, and for eight of the ten cells the deviations are less than  $2^{\circ}$  C. ( $4^{\circ}$  F.). This agreement is very satisfactory.

The deviations of Fig. 12 do not correspond to the deviations from linear response shown in Figs. 8 and 9. This result is to be expected, since the calibration is affected by the spectral distribution of sensitivity as well as by the deviation from linear response.

It may be concluded that the standard Table given in Appendix I. will give with sufficient accuracy the calibration of any of the ten cells, provided that the current corresponding to any one temperature is known. Apart from cell *L*, which seems to be defective, the variation of mean sensitivity of the cells corresponds to  $\pm 4^{\circ}$ .

TABLE III.—*Comparison of Thermocouple and Photo-Cell Readings.*

Thermocouple. ° C.	Photo-Cell. ° C.	Difference. ° C.	Thermocouple. ° C.	Photo-Cell. ° C.	Difference. ° C.
<i>Cell A.</i>					
1176½	1172	-4½	1182½	1181	-1½
1312½	1307	-5½	1301	1296	-5
1397	1393½	-3½	1398½	1391½	-7
1456	1454	-2	1445	1438	-7
1553½	1553	-½	1576	1569	-7
1592	1590	-2			
<i>Cell B.</i>					
1186	1182½	-3½	1194½	1188	-6½
1306	1301½	-4½	1310	1303	-7
1403	1396½	-6½	1410	1404	-6
1441	1436	-5	1440	1435	-5
1586½	1579½	-7	1592	1588½	-3½
<i>Cell C.</i>					
1186	1182½	-3½	1194½	1188	-6½
1306	1301½	-4½	1310	1303	-7
1403	1396½	-6½	1410	1404	-6
1441	1436	-5	1440	1435	-5
1586½	1579½	-7	1592	1588½	-3½
<i>Cell D.</i>					

at  $1400^{\circ}$  C. ( $\pm 7^{\circ}$  at  $2550^{\circ}$  F.) or  $\pm 6^{\circ}$  at  $1700^{\circ}$  C. ( $\pm 11^{\circ}$  at  $3090^{\circ}$  F.). If an occasional error of  $10^{\circ}$  C. ( $18^{\circ}$  F.) could be tolerated the Table could be used for the nine cells without any corrections.

In order to make the two standard Tables consistent, the black-body Table was calculated from the tungsten-lamp Table by the method described in Part I. of the paper. It is therefore of particular interest to see how far the Table agrees with the experimental calibration against a platinum thermocouple in a black-body furnace. The results of the experiments are summarised in Table III. The details of the calibration of one cell are given in Table XI., Appendix II. The photo-electric pyrometer read fairly consistently  $5^{\circ}$  C. lower than the thermocouple over the whole temperature scale. This might be due to imperfect black-body conditions, to

errors in the calibration of the thermocouple or of the lamp, or to a combination of these factors. The discrepancy is within the experimental error.

### *Measuring Circuit Resistance.*

The resistance of the measuring circuit affects all the properties of a barrier-layer cell. For most cells the fatigue is greater for higher resistances, but a resistance of 1000 ohms does not increase the fatigue by more than about 20%. The effect of the resistance on the temperature coefficient has already been discussed. The departure from linear response—and consequently also the calibration—is affected by the resistance to a degree determined by the intensity of illumination. This point is illustrated in Fig. 13,

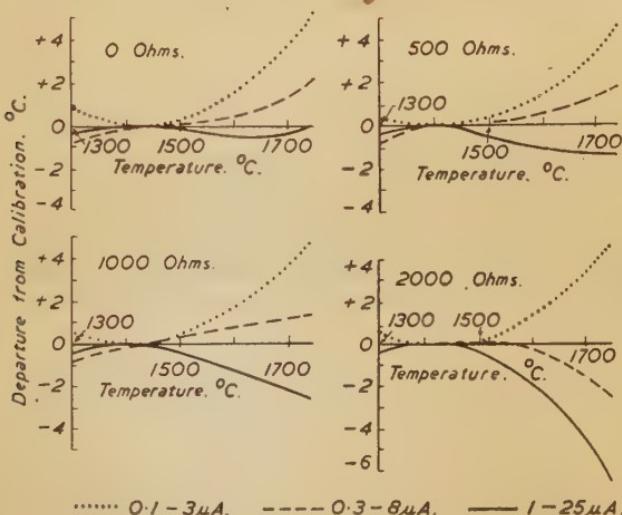


FIG. 13.—Effect of the Intensity of Illumination and of the Measuring Circuit Resistance on the Calibration.

which shows the departure of a cell from the standard calibration for different intensities of illumination and different resistances in the measuring circuit. Each curve has been drawn to pass through zero difference at  $1450^{\circ}$  C. The calibration for a low intensity of illumination is practically unaffected by the resistance up to 2000 ohms. A medium illumination shows a small change of calibration with resistance, and for high illumination and a resistance of 2000 ohms the departure from the standard curve is serious. For currents of about 10 micro-amp. a resistance of 1000 ohms is usually quite satisfactory.

### *Variations of Dimensions of Pyrometer.*

In the theoretical section of the paper (Part I.) it was shown that the cell current should be proportional to  $A_l A_c / d^2$ , where  $A_l$  and  $A_c$  are respectively the areas of the lens stop and the cell stop

and  $d$  is the distance between them. The effect of varying each of the three factors was studied.

The area of the cell stop was varied from 0.2 sq. cm. to 1.7 sq. cm. (using a 25-mm. cell), and the results are given for four cells in Table IV.

TABLE IV.—*Influence of Area of Cell Stop.*

Aperture, Sq. cm.	Deviation from Standard Table. %.			
	Cell A.	Cell B.	Cell C.	Cell D.
0.192	-1½	+1	+3	-1
0.795	-1	+1	+½	+1
0.994	-2	+1	+1	0
1.745	-3½	+2	-2	-3½

Differences of up to 5% are apparent, but no very definite trend can be noticed. The variation of the sensitivity of different parts of the surface of a cell was measured, using a small spot of light, and variations of the same magnitude were found. The variation is therefore chiefly due to the inhomogeneity of the sensitive surface.

The effect of varying the lens aperture is seen in Table V. Two different lenses were used, one of 5 cm. and the other 10 cm. focal length.

TABLE V.—*Effect of Area of the Lens Aperture.*

Focal Length of Lens, Cm.	Area of Lens Stop ( $A_1$ ). Sq. cm.	Aperture.	Cell Current ( $i$ ). Micro- amp.	$\frac{i}{A_1}$ .	Percentage Difference from Normal.
5	0.321	f/7.8	0.464	1.443	— 2.3
5	0.723	f/4.7	1.068	1.475	0.0
5	2.03	f/3.1	3.030	1.492	+ 1.2
5	5.09	f/2.0	6.489	1.275	-13.6
10	0.321	f/15.6	0.460	1.432	— 2.9
10	0.723	f/9.4	1.056	1.459	— 1.1
10	2.03	f/6.2	2.942	1.450	— 1.7
10	5.09	f/3.9	7.205	1.416	— 4.0

The 5-cm. lens gives a current approximately 1½% greater than the 10-cm. lens; this is probably due to its thickness. It is rather surprising to find that the cell current increases in proportion to the lens aperture even up to f/3. The largest aperture gives a current noticeably too low, as might be expected, but it is unexpected to find the smallest aperture giving a low current. The variations, however, do not exceed an overall total of 3% for either lens, and are not excessive.

The effect of varying the distance between the stops is seen in Fig. 14. The ordinate is the variation of the product  $id^2$ . The deviation of the cell current from linear response, measured under the same conditions by the inverse-square method, is shown (dashed)

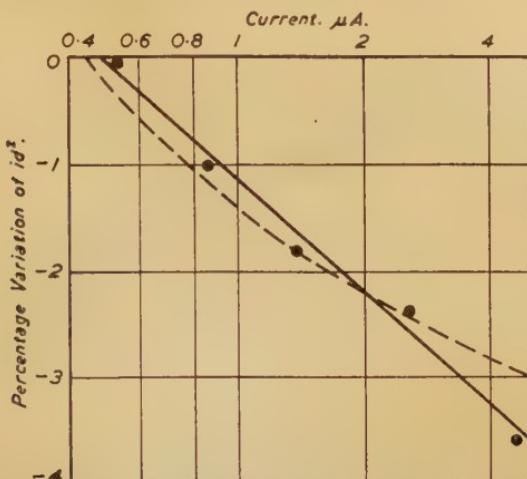


FIG. 14.—Variation of Cell Current ( $i$ ) with Distance ( $d$ ) between Stops.  
Broken line is the departure from linear response of the cell.

on the same graph. The two curves are almost parallel, and the effect of varying the distance between the stops seems to follow the inverse-square law almost exactly. The experiment was repeated with other lenses and lens stops, and the results fell very exactly along the same line.

#### *Use of a Heat-Absorbing Filter.*

In view of the importance of maintaining the cell at a reasonably low working temperature ( $40^\circ$  C. ( $105^\circ$  F.) is about the limit), it was thought advisable to investigate the effect of filters which absorb radiant heat. Such filters should be particularly valuable when using the photo-electric cell to measure low temperatures.

Although water is a very convenient medium for absorbing radiant heat in laboratory work, it is scarcely desirable in industrial equipment. The most suitable filter is probably a heat-absorbing glass, and experiments were made using a  $\frac{1}{4}$ -in. thick plate of "Calorex" glass, kindly lent by the Glass Technology Department of the University of Sheffield. The spectral transmission of this glass at different temperatures is shown in Fig. 15, which is taken from a paper by Holland and Turner.<sup>(16)</sup> The transmission of radiant heat was measured by means of a radiation pyrometer sighted on a furnace. The transmission of radiant heat was found to be 7.8% at a furnace temperature of  $1200^\circ$  C. and 9.1% at  $900^\circ$  C.

The reduction in response of the photo-electric cell and the change in calibration are given in Table VI. It will be seen that the filter has the effect of reducing the cell current to about half, and making

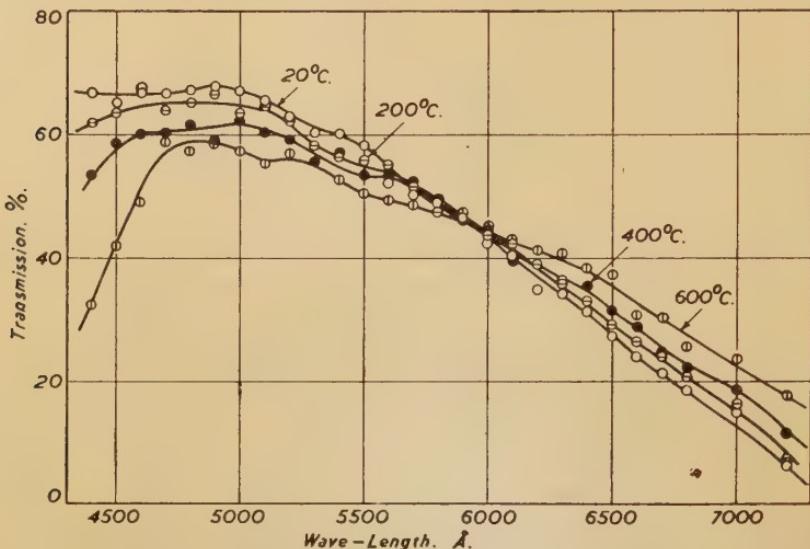


FIG. 15.—Effect of Temperature on the Spectral Transmission of Calorex Glass No. 26 (thickness,  $\frac{1}{4}$  in.). (Holland and Turner<sup>(16)</sup>).

the calibration curve a little steeper, the standard current being increased by an amount corresponding to about  $7^\circ\text{ C.}$  at  $1700^\circ\text{ C.}$  ( $12^\circ\text{ F.}$  at  $3090^\circ\text{ F.}$ ), and decreased by a similar amount at  $1400^\circ\text{ C.}$  ( $2560^\circ\text{ F.}$ ), relative to the calibration at  $1560^\circ\text{ C.}$  ( $2840^\circ\text{ F.}$ ).

TABLE VI.—Influence of Heat-Absorbing Filter on Response and Calibration of a Photo-electric Cell.

Temperature.	Cell Current. $\mu\text{A.}$		Transmission of Filter.	Change of Calibration Relative to $1560^\circ\text{ C.}$
	Without Filter.	With Filter.		
$1400^\circ\text{ C.}$ ( $2560^\circ\text{ F.}$ )	0.654	0.289	0.442	$-7^\circ\text{ C.}$ ( $-12^\circ\text{ F.}$ )
$1560^\circ\text{ C.}$ ( $2840^\circ\text{ F.}$ )	2.313	1.073	0.464	...
$1700^\circ\text{ C.}$ ( $3090^\circ\text{ F.}$ )	5.914	2.861	0.485	$+7^\circ\text{ C.}$ ( $+12^\circ\text{ F.}$ )

#### Value of Effective Wave-length.

The effective wave-length of the cell can be calculated from the shape of the calibration curve, from the difference between the calibrations for black-body radiation and the tungsten lamp, and from the spectral distribution of sensitivity. We have seen that the first two methods are in reasonably good agreement.

The values of the effective wave-length as calculated from the spectral-sensitivity curve are given in Table VII., together with the

TABLE VII.—*Effective Wave-Lengths of Cells.*

Temperature.	Effective Wave-Length. Microns.	
	From Spectral Sensitivity.	From Calibration.
1300° C. (2372° F.)	0·612	0·611
1500° C. (2732° F.)	0·604	0·599
1700° C. (3052° F.)	0·599	0·590

values calculated from the calibration curves. The spectral-sensitivity curve used was supplied by the manufacturers of the cells. The agreement is quite as good as could be expected from the accuracy of the standards of temperature available.

### *Conclusions.*

The experimental results show that the barrier-layer cells tested are quite suitable for the industrial measurement of high temperatures. Care must be taken with fatigue and temperature coefficients. The response of a cell declines by an amount which, under adverse conditions, may correspond to as much as 10° at 1700° C. (18° at 3100° F.). At least half of the change occurs during the first minute, and after an hour's illumination the response is very steady. The normal seasonal variation of atmospheric temperature in Great Britain may be taken as about 25° C. (45° F.). With some cells this may cause changes of  $\pm 5^\circ$  C. ( $\pm 9^\circ$  F.) in the calibration. The error from this source can usually be reduced by including a suitable resistance in the measuring circuit; but care must be taken that the resistance is not large enough to alter the calibration of the cell.

The relative cell currents for different temperatures of the hot source seem to be very nearly the same for all the cells. A standard Table (Table VIII A., Appendix I.) represents the calibrations of the cells within limits which rarely exceed 2° C. (4° F.) over the temperature range 1350–1750° C. (2460–3180° F.). An extended source of black-body radiation is rarely available, but a tungsten-ribbon-filament lamp may be used to calibrate the cells, provided that allowance is made for the difference in effective wave-length between the cell and the optical pyrometer used to calibrate the lamp. The correction is included in Table VIII B. When the cell is calibrated in this way it may be necessary to use a different optical system for calibration from that employed in the pyrometer. The calculation of the effect of changing the optical system rests on certain simple geometric relations, and experiment shows that it should not involve an error of more than a few degrees.

The cells were obtained in three batches, which seemed equally good, but one cell was distinctly abnormal in its fatigue properties. This suggests that variations in manufacture may still occur and that some batches may not be up to the standard of the cells tested. It is clear, however, that good cells can be produced and suitable selection should ensure satisfactory results.

### APPENDIX I.—Tables of $\log_{10} i_s$ .

Table VIII. gives the values of the logarithm of the "standard current" (in micro-amperes) at different temperatures, expressed in reciprocals of absolute temperature, when a single lens is interposed between the source and the cell. The reciprocal of any absolute temperature may be derived from the corresponding centigrade or Fahrenheit temperature by using Table IX. or Table X. To find the current for given dimensions of apertures the standard current must be multiplied by  $A_l A_c / d^2$ , where all lengths are measured in centimetres. Individual cells may be rather more or less sensitive than the "average cell" to which the Tables apply, so that the current from any particular cell may differ from the Tables by a factor usually in the region of 0.95–1.05, which will be the same for all temperatures.

TABLE VIII.— $\log_{10} i_s$ .

$\frac{10^4}{T}$	0.0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
A.—Black Body.										
5	4.373	4.268	4.164	4.060	3.957	3.854	3.751	3.648	3.546	3.444
6	3.343	3.241	3.140	3.039	2.938	2.838	2.739	2.640	2.541	2.442
B.—Tungsten Lamp (Calibrated at 0.66 $\mu$ ).										
5	4.420	4.314	4.209	4.104	4.000	3.896	3.792	3.688	3.584	3.481
6	3.378	3.275	3.173	3.071	2.969	2.868	2.767	2.666	2.566	2.466

### APPENDIX II.—Details of Calibration of Cell D against a Platinum/Platinum-Rhodium Thermocouple in a Black-Body Furnace.

The thermocouple e.m.f. (column 1, Table XI.) is corrected to the cold-junction value at 0° C. The deviation of the cell calibration from Table VIII B. (column 5) was determined by a separate experiment using the same cell stop.

Lens aperture ( $A_l$ ) . . . . .	0.958 cm. in dia.
Cell aperture ( $A_c$ ) . . . . .	0.191 sq. cm.
Distance between stops ( $d$ ) . . . . .	19.55 cm.

$$s = \frac{A_l A_c}{d^2}$$

$$\text{hence } \log_{10} s = 4.558$$

TABLE IX.—*Centigrade Reciprocal Table.*

Temp. °C.	Reciprocals of Absolute Temperatures, $\frac{10^4}{T}$ .									Difference Table.									
	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	1.	2.	3.	4.	5.	6.	7.	8.	9.
1200	6.789	6.743	6.698	6.653	6.610	6.566	6.523	6.481	6.439	6.398	4	9	13	18	22	27	31	35	40
1300	6.357	6.317	6.277	6.238	6.200	6.162	6.124	6.086	6.049	6.013	4	8	11	15	19	23	27	30	34
1400	5.977	5.942	5.907	5.872	5.838	5.804	5.770	5.737	5.704	5.672	3	7	10	13	17	20	24	27	30
1500	5.640	5.608	5.577	5.546	5.516	5.485	5.455	5.425	5.397	5.368	3	6	9	12	15	18	21	24	27
1600	5.339	5.311	5.283	5.255	5.228	5.200	5.173	5.147	5.120	5.094	3	5	8	11	14	16	19	22	24
1700	5.069	5.043	5.018	4.993	4.968	4.943	4.919	4.895	4.871	4.847	2	5	7	10	12	15	17	20	22

TABLE X.—*Fahrenheit Reciprocal Table.*

Temp. °F.	Reciprocals of Absolute Temperature, $\frac{10^4}{T}$ .									Difference Table.									
	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	1.	2.	3.	4.	5.	6.	7.	8.	9.
2200	6.769	6.743	6.718	6.693	6.668	6.644	6.620	6.596	6.570	6.546	2	5	7	10	12	15	17	20	22
2300	6.523	6.500	6.477	6.453	6.430	6.408	6.385	6.362	6.340	6.317	2	5	7	9	11	14	16	18	21
2400	6.295	6.273	6.251	6.229	6.208	6.187	6.166	6.145	6.124	6.103	2	4	6	9	11	13	15	17	19
2500	6.082	6.061	6.041	6.021	6.001	5.981	5.962	5.942	5.922	5.903	2	4	6	8	10	12	14	16	18
2600	5.883	5.864	5.846	5.827	5.808	5.789	5.770	5.752	5.734	5.715	2	4	6	7	9	11	13	15	17
2700	5.697	5.680	5.662	5.643	5.626	5.608	5.591	5.574	5.556	5.539	2	3	5	7	9	10	12	14	16
2800	5.523	5.506	5.489	5.472	5.455	5.439	5.423	5.407	5.390	5.374	2	3	5	7	8	10	12	13	15
2900	5.358	5.342	5.327	5.311	5.296	5.280	5.264	5.249	5.234	5.219	2	3	5	6	8	9	11	13	14
3000	5.203	5.188	5.173	5.159	5.144	5.129	5.114	5.100	5.086	5.072	1	3	4	6	7	9	10	12	13
3100	5.058	5.043	5.029	5.015	4.991	4.988	4.974	4.960	4.946	4.932	1	3	4	6	7	8	10	11	13

TABLE XI.—*Details of Calibration of Cell D.*

1 Thermo-couple E.m.f. M.V.	2 Temp. of Furnace. ° C.	3 Cell Current, i. Micro- amp.	4 $\log_{10} \frac{i}{s}$ .	5 Deviation of Cell from Table VIIIB, $\log_{10} c$ .	6 $\log_{10} \frac{i}{sc}$ .	7 $\frac{10^4}{T}$ from Col. 6 and Table VIIIA.	8 Temp. as measured by Cell. ° C.	9 Difference between Col. 2 and Col. 8. ° C.
13-16	1194½	0.117	2.510	+0.014	2.496	6.845	1188	-6½
13-20	1197	0.120	2.521	+0.014	2.507	6.834	1190	-7
14-78	1310	0.362	3.001	+0.007	2.994	6.345	1303	-7
14-79	1311	0.366	3.005	+0.007	2.998	6.341	1304	-7
16-15	1408	0.847	3.370	0.000	3.370	5.973	1401	-7
16-18	1410	0.868	3.381	0.000	3.381	5.962	1404½	-5½
16-25	1415½	0.917	3.404	0.000	3.404	5.940	1410½	-5
16-60	1440	1.118	3.490	-0.001	3.491	5.854	1435	-5
16-62	1441½	1.135	3.497	-0.001	3.498	5.847	1437	-4½
18-68	1591	3.431	3.977	-0.003	3.980	5.378	1587	-4
18-70	1592	3.482	3.984	-0.003	3.987	5.371	1589	-3

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[This paper was discussed jointly with the preceding one by D. Manterfield on "Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces" and the following three by D. A. Oliver and T. Land on "A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures," by D. J. Price and H. Lowery on "The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red" and by J. A. Hall on "The Drift of Selenium Photo-Electric Cells in Relation to their Use in Temperature Measurement."]



# A THERMOCOUPLE METHOD FOR THE MEASUREMENT OF LIQUID STEEL CASTING-STREAM TEMPERATURES.<sup>1</sup>

BY D. A. OLIVER, M.Sc., F.Inst.P., AND T. LAND, M.A. (RESEARCH DEPARTMENT, MESSRS. WILLIAM JESSOP & SONS, LTD., SHEFFIELD).

(Figs. 7 to 10 = Plates XXXIV. and XXXV.)

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## SUMMARY.

A new method of measuring the true temperature of the liquid steel in the casting stream is described. A platinum/platinum-rhodium thermocouple, lightly sheathed in silica, was allowed to protrude into the narrow part of the conical refractory lining of a runner box. The e.m.f. of the thermocouple was applied to a mains-driven high-speed amplifier and recorder, which showed that a steady temperature was attained in approximately 15 sec. The application of the method is illustrated by two investigations. The first was on the emissivity of a nickel-chromium-molybdenum steel, which was deduced from the comparison of optical pyrometer readings and the true temperatures measured by the thermocouple. In the second investigation thermocouple readings of the ladle stream temperature were compared with the recorded temperatures of the metal in the furnace before tapping, from which the ladle cooling of the liquid steel was deduced. The results showed gratifying consistency and the procedures proved simple and reliable.

## INTRODUCTION.

THE influence of casting temperature on the quality of ingots and foundry castings is widely recognised, and in many steelworks and foundries routine observations on the casting stream are made with optical pyrometers. Such measurements are made for record purposes rather than for temperature control, so that the repetition of unsuitable temperature conditions may be avoided.

The optical pyrometer has given good service in the foundry with which the authors are particularly concerned, but its accuracy is severely limited. The temperature measured with an optical pyrometer is not the true temperature of the metal, and a correction of about 130° C. (235° F.) is usually added to the pyrometer reading. The reading obtained depends not only on the temperature of the metal but also on such factors as the steel composition, the degree of oxidation of the surface and the smoke which may be present

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between the metal stream and the observer. It is clearly desirable to devise a more accurate method of measurement, either to supersede the optical pyrometer or at least to give under experimental conditions more exact information about the correction to be applied to optical-pyrometer readings in different circumstances.

When the metal is poured over the lip of a ladle, the normal quick-immersion technique using a platinum thermocouple is quite satisfactory, and accurate temperature measurements can readily be made. When the metal is bottom-poured, however, the velocity of the moving stream is such that any tube put into the stream merely splays metal in all directions. It is clearly necessary to measure the temperature at some point where the metal flow is unimpeded and is constricted by a short tubular ring. The present paper describes the development of a method based on this principle.

#### EARLY ATTEMPTS TO MEASURE CASTING-STREAM TEMPERATURES.

The first "temperature ring" was made of arc-furnace electrode graphite, and the details are shown in section in Fig. 1. The thermocouple was protected by a silica tube, which projected about one inch from the graphite in the narrow part of the funnel. The graphite ring was mounted in a stout steel frame (Fig. 7), so that it could be placed on a casting box over an ingot for the preliminary experiments.

The greater part of the ingot was cast straight through the casting box, without passing through the graphite funnel; when the metal in the ingot reached the ingot head, the ladle was moved across and the remainder of the steel was cast through the "temperature ring." The thermocouple was connected to a Tinsley high-speed amplifier and recorder, and the record obtained is shown in Fig. 2, which also records the previous dip in the furnace and (unsuccessfully) in the launder.

The results were most encouraging, although several possible improvements

were apparent. The silica sheath survived intact, although it was somewhat bent, and the thermocouple was undamaged. The graphite ring was considerably eroded by the flowing metal, and some alternative material seemed to be indicated.

As a result of the first experiment a new assembly was tried. It consisted of a "trumpet top" attached to a 2-in. ladle nozzle (Fig. 8). This combination was built into a sand mould in place of the usual runner-box. The nozzle was drilled with a  $\frac{1}{4}$ -in. hole at an angle of about  $35^\circ$  to the horizontal, and a silica tube containing

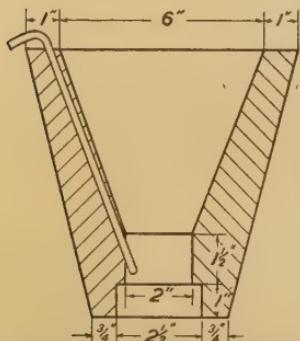


FIG. 1.—Section of Graphite Funnel with Thermocouple in Position.

the thermocouple wires was introduced through the hole, protruding  $\frac{3}{4}$  in. into the casting stream. When the steel was cast the silica sheath was broken and no reading was obtained. However, later

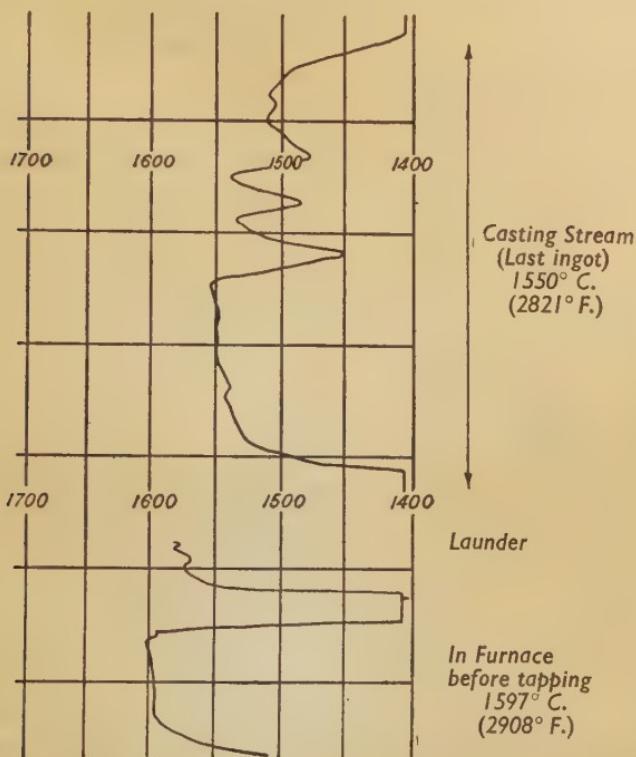


FIG. 2.—Tracing of First Record of True Casting-Stream Temperature.

experiments suggested that this assembly with slight modifications might still prove suitable for casting-stream measurements on up-hill cast ingots.

#### FINAL DESIGN OF APPARATUS.

The early attempts suggested a design which has given very good results. The basis was a standard runner-box, rammed with "compo," consisting of a conical refractory lining,  $\frac{3}{4}$  in. thick, 10 in. deep, tapering to a minimum internal diameter of  $2\frac{1}{2}$  in., and provided with a cylindrical cast-iron case. The refractory lining was drilled 1 in. from the bottom with a  $\frac{1}{4}$ -in. hole at an angle of about  $35^\circ$  to the horizontal, and a 1-in. hole was drilled at the appropriate point in the cast-iron case. The two components of the runner-box were assembled with a steel rod in place of the thermocouple tube, rammed with compo and dried out. The complete assembly is shown in section in Fig. 3 and viewed from above in Fig. 9.

The thermocouple tube was a silica sheath  $4\frac{3}{4}$  in. long,  $6\frac{1}{2}$  mm. in external diameter and 0.7 mm. in wall thickness. The platinum/platinum-rhodium thermocouple wire was 0.5 mm. in dia. and insulated in fine twin-bore silica tubing. The head of the thermocouple unit was a standard two-way porcelain connector cemented to the silica tube. The thermocouple unit could be placed in the runner-box just before casting; it was held in position with a little "Sairset" cement. About  $\frac{3}{4}$  in. of the silica tube protruded into the casting stream. It was quickly found advisable to cover the thermocouple head and about a foot of the compensating lead attached to it with asbestos tubing to protect them from splashes of hot metal. The runner box and thermocouple assembly are seen in position on a mould in Fig. 10.

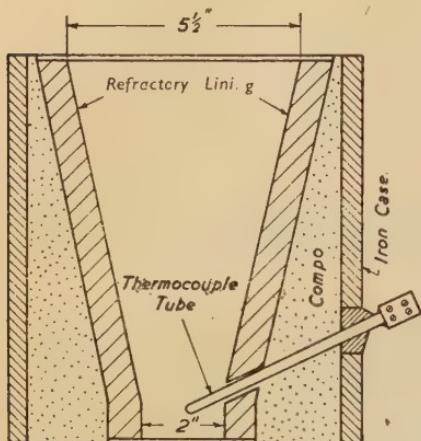


FIG. 3.—Section of Runner-Box adapted to take Thermocouple.

It was found that about two out of three determinations were satisfactory with this arrangement, the chief cause of failure being that the ladle operator sometimes interrupted the casting stream during casting, so that the thermocouple did not reach a steady temperature. Occasionally the silica tube broke or the bending of the tube caused a short-circuit in the thermocouple, but the majority of observations were quite satisfactory. Typical records are shown in Figs. 4 and 5.

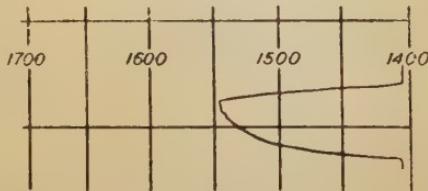


FIG. 4.—Tracing of First Record of Casting-Stream Temperature using Adapted Runner-Box.

A conical refractory lining as used in the runner-box has been fitted in the steel frame shown in Fig. 7 and used successfully to measure the casting-stream temperature during the casting of an ingot. A difficulty which sometimes arises in such measurements is that the swinging of the ladle may cause the thermocouple to be

momentarily exposed every few seconds, so that it never reaches a steady temperature. This trouble can be overcome by steadying the ladle with long poles, as is usually done in the foundry.

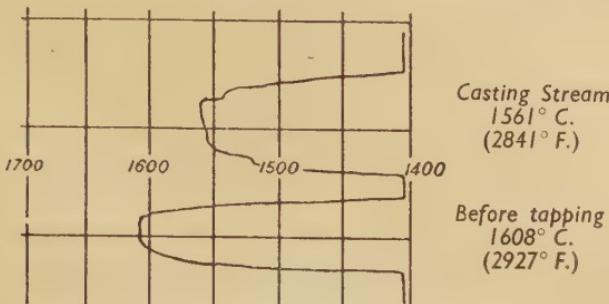


FIG. 5.—Tracing of Typical Pair of Records showing Furnace Temperature and Casting-Stream Temperature.

### *Accuracy.*

The accuracy depends first on the thermocouple being immersed in the liquid steel for a sufficient time to enable it to attain a steady temperature. In Fig. 4 the time (12 sec.) was scarcely long enough, but in Fig. 5 15 sec. sufficed to give a perfectly satisfactory record. It appears that the method in its present form is applicable only to castings of greater weight than 5 cwt.

Another possibility of error is that the refractory lining may cool the steel before it reaches the thermocouple. Approximate calculations suggest that the cooling is unlikely to exceed 3° C. (6° F.) for the 7-cwt. castings investigated, and is more likely to be less than 2° C. (4° F.). This source of error has therefore been neglected.

In quick-immersion temperature measurements in the furnace it is usually considered necessary for the silica sheath to be immersed for at least  $1\frac{1}{2}$  in. from the hot junction to obviate errors due to heat conduction towards the cool part of the sheath. The greater efficiency of heat transfer in a fast-moving stream appears to reduce this depth of immersion considerably, and  $\frac{3}{4}$  in. of tube protruding into the flowing stream appears to be adequate.

The accuracy of the combined amplifier and recorder is of a high order ( $\pm 2^\circ$  C. or  $\pm 4^\circ$  F.). The constancy of the amplification depends only on the permanence of a single resistor, and the overall precision is checked by reference to a Weston standard cell incorporated in the amplifier.

### APPLICATIONS.

To illustrate the value of the method a series of measurements was made using the "temperature ring" and simultaneously observations were made with a calibrated disappearing-filament optical pyrometer. Temperature measurements were also made in

the furnace before tapping. In this way the emissivity and the ladle cooling of the steel were measured, two quantities of particular interest to the Foundry Steel Temperature Sub-Committee.

The measurements were made on a nickel-chromium-molybdenum steel which was, at the time of these experiments, in regular production under closely standardised conditions. A typical analysis was as follows.

Carbon . . .	0·40% by weight.	Nickel . . .	2·5% by weight.
Manganese . . .	0·60% " "	Chromium . . .	0·80% "
Silicon . . .	0·25% " "	Molybdenum . . .	0·65% "

The steel was made in a 12-ton basic electric-arc furnace, and cast from a ladle lined with fireclay bricks. The metal was poured

TABLE I.—Temperature Measurements in the Furnace and during Casting.

Cast No.	Time.	Furnace Dip. ° C.	Power. K.W.	Tapped. Time.	Casting.			Remarks.
					No.	Ring Couple. ° C.	Optical. ° C.	
A498	11·18	1625	...	...	3	1560	1435	
A510	11·15	1600	1050	11·28	3	1570	1422	
A520	11·56	1623	600	12·12	3	1550	1390	
A528	9·55 10·06 10·21	1592 1619 1621	1000 1000	10·25	3 6	1560 1562	1420 1420	Ladle about 600° C.
C429	11·39 11·50	1580 1602	1500 1500	11·53	3	1560	1425	
A537	11·46 11·56	1610 1603	900 1250	12·03	3	1555	1438	0·30% carbon steel.
A539	13·03 13·15	1560? 1615	1400 1200	13·22	5	1562-1568	1418	0·30% carbon steel.
A541	11·25 11·36	1580-1592 1617	1200 750	11·47	3 7	1555 1555	1420 1415	

from the bottom of the ladle through a magnesite nozzle with a fire-clay stopper end, previously boiled in tar.

The optical pyrometers, manufactured by the Cambridge Instrument Company and by Hartmann and Braun were calibrated within 24 hr. of each observation against a tungsten ribbon-filament lamp standardised at the National Physical Laboratory. The ladle was heated by a gas burner to a temperature of approximately 650° C. (1200° F.) before tapping. The metal was held in the ladle for 10 min. before casting. The majority of observations were taken on the third 7-cwt. casting.

The experimental results are given in Table I.

*Emissivity.*

The emissivity of liquid steel is the ratio of the radiant energy emitted per unit area of the steel surface to the energy radiated by a perfect black body at the same temperature. Since the human eye in conjunction with the red filter of the optical pyrometer only responds to radiation in a narrow band of wave-lengths, the emissivity ( $E_\lambda$ ) with which we are concerned is the "spectral emissivity" at the effective wave-length ( $\lambda_e$ ) of the optical pyrometer. The effective wave-length was approximately 0.65 micron. The relation between true temperature ( $T$ ) and apparent temperature ( $T_{app}$ ) is given by :

$$\frac{C_1}{\lambda_e^5} e^{-\frac{C_2}{\lambda_e T_{app}}} = E_\lambda \cdot \frac{C_1}{\lambda_e^5} e^{-\frac{C_2}{\lambda_e T}},$$

$$\therefore \frac{1}{T} - \frac{1}{T_{app}} = \frac{\lambda_e}{C_2} \log_e E_\lambda,$$

where  $C_1$  and  $C_2$  are Wien's radiation constants. It was not always practicable to make a temperature measurement in the furnace immediately before tapping the metal into the ladle. The relation between the power input to the furnace as indicated on the watt-

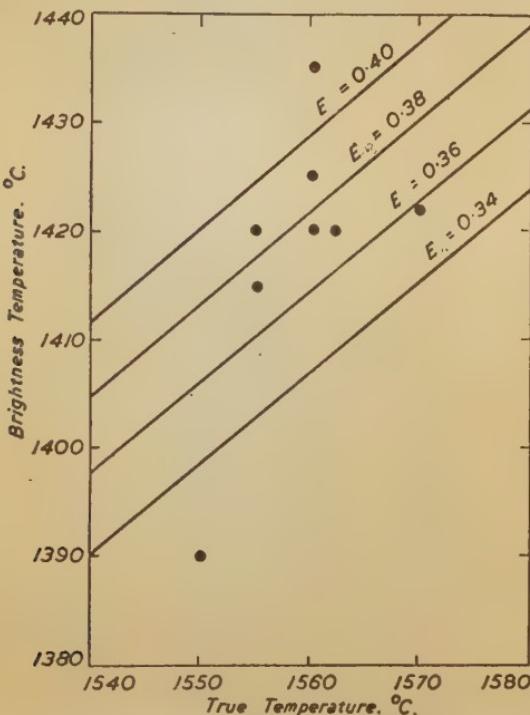


FIG. 6.—Relation between Brightness Temperature (as Measured by Optical Pyrometer) and True Casting-Stream Temperature for Nickel-Chromium-Molybdenum Steel.

meter and the rate of rise of temperature had previously been determined as accurately as possible; this relation was used to estimate the true temperature of the metal as it left the furnace. In most cases the furnace was tapped within 10 min. of the last dip measurement in the furnace, and the estimated temperature change during the period was between 3° and 17° C. (5° and 31° F.).

The measurements of the true casting-stream temperature measured by the authors' new method and of the brightness temperature measured optically are correlated in Fig. 6. The majority of the observations lie in the neighbourhood of the line corresponding to an emissivity of 0·38. The only point seriously out of accord is that for a brightness temperature of 1390° C. (2534° F.). It seems probable that there was interference with the optical reading due to smoke during this observation. The correlation is quite as good as could be expected, merely taking into account the uncertainty of the optical-pyrometer readings, which are rarely reliable to better than  $\pm 10^\circ$  C. ( $\pm 18^\circ$  F.).

#### *Ladle Cooling.*

Ladle cooling readings obtained with the alloy steel are set out in Table II., which also includes two results on carbon steels (A537 and A539). The ladle was of normal design capable of holding 14 tons of molten steel. In these experiments the average content of metal was approximately 10 tons.

TABLE II.—*Ladle Cooling Readings.*

Cast No.	Tapping Temp. °C.	Casting-Stream Temp. °C.	Ladle Cooling. °C.
A510 . . . .	1617	1570	47
A520 . . . .	1620	1550	70
A528 . . . .	1626	1561	65
C429 . . . .	1608	1560	48
A537 . . . .	1615	1555	60
A539 . . . .	1627	1565	62
A541 . . . .	1622	1555	67

The average value of the temperature drop between furnace and ladle was 60° C. (108° F.), the range of variations being 23° C. (41° F.), i.e.,  $\pm 12^\circ$  C. ( $\pm 22^\circ$  F.). The authors have pointed out in a previous paper<sup>1</sup> that there is likely to be this range of uncertainty in furnace temperature measurements; in addition there is an uncertainty of at least 5° C. (9° F.) in estimating the change in temperature between the last dip measurement in the furnace and the commencement of tapping. The results therefore can be considered concordant within anticipated limits.

<sup>1</sup> Oliver and Land, *Journal of The Iron and Steel Institute*, 1942, No. I., pp. 245 p-259 p.

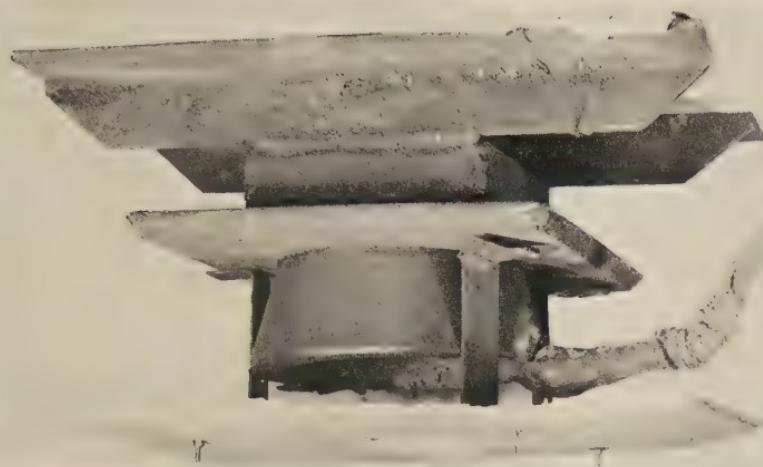


FIG. 7.—Graphite Funnel in Steel Frame as used on Ingot Mould.



FIG. 8.—Improvised Refractory Funnel with Thermocouple in Position.

[*Oliver and Land.*  
[To face p. 520 P.



FIG. 9.—Runner-Box Head after Use, showing silica tube protruding.



FIG. 10.—Mould with Special Runner-Box, showing compensating lead.

[*Oliver and Land.*  
[To face p. 521 p.]

One of the authors<sup>1</sup> has published a mathematical analysis of the ladle cooling of liquid steel, stating that the figures given in the paper should be multiplied by a constant factor to be determined experimentally. The value of the ladle cooling calculated from the published tables is 78° C. (140° F.) for the conditions of the experiments, so that the constant factor in this case is 0.7. It remains to be seen, however, whether this value is equally valid for a wide range of conditions.

#### CONCLUSIONS.

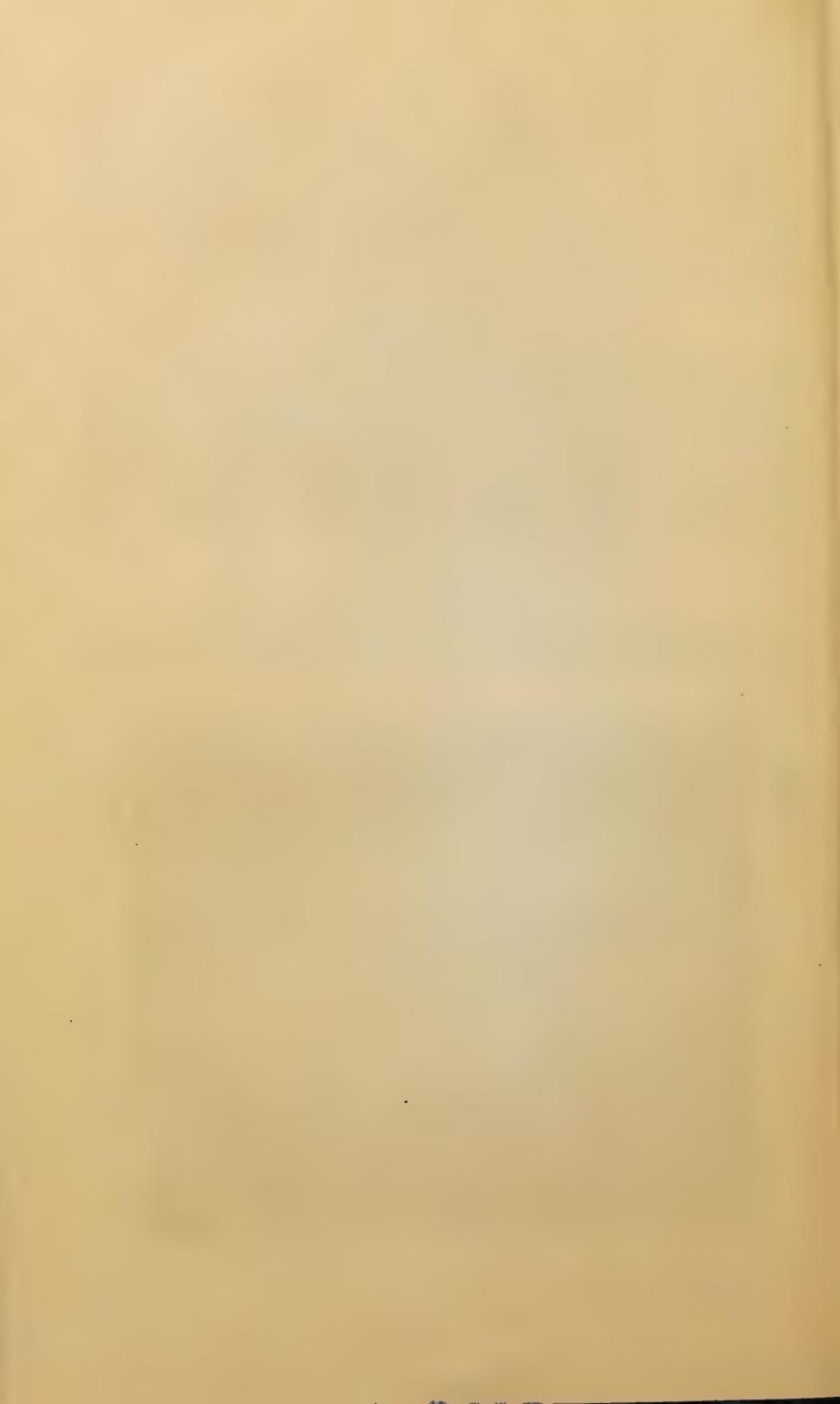
A simple and successful method has been devised for measuring the temperature of the casting stream in the foundry. It can be applied to castings of more than 5 cwt. in weight with only slight modification of standard foundry practice. It appears essential to employ some type of high-speed temperature recorder in view of the short time available for the measurement. The method appears to be suitable for the investigation of emissivities and the ladle cooling of liquid steels under foundry conditions.

#### ACKNOWLEDGEMENT.

The authors are indebted to the members of the Foundry Steel Temperature Sub-Committee for helpful discussion during the course of this investigation.

<sup>1</sup> Land, *Journal of The Iron and Steel Institute*, 1941, No. II., pp. 157 p-168 p.

[This paper was discussed jointly with the preceding two by D. Manterfield on "Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces" and by T. Land on "Barrier-Layer Photo-Electric Cells for Temperature Measurement" and the following two by D. J. Price and H. Lowery on "The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red" and by J. A. Hall on "The Drift of Selenium Photo-Electric Cells in Relation to their Use in Temperature Measurement."]



# THE EMISSIVITY CHARACTERISTICS OF HOT METALS, WITH SPECIAL REFERENCE TO THE INFRA-RED.\*

BY D. J. PRICE, B.Sc., A.INST.P., AND H. LOWERY, D.Sc., F.INST.P.  
(SOUTH-WEST ESSEX TECHNICAL COLLEGE, WALTHAMSTOW, LONDON).

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## SUMMARY.

The theoretical and practical considerations in connection with the study of emissivity are discussed and the relevant literature is critically surveyed. The application of emissivity data to the correction of pyrometer readings has been examined and the necessity of an adequate knowledge of emissivity data is indicated. The information at present available does not meet this need, especially in the important case of iron, and, in view of this, suggestions for future experimental researches are noted.

Correlation of all available data appears to indicate a zero temperature coefficient of emissivity (for all substances) at a specific wave-length in the infra-red region. This implies that at a certain wave-length peculiar to each substance the emissivity correction to a pyrometer would take a much simpler form than at present.

## INTRODUCTION.

THE investigation of the spectral energy radiated by solid and liquid metals at high temperatures is of double interest: First, the measurement of radiation in both the visible and the infra-red portions of the spectrum seems to be the simplest method for determining high temperatures, provided that the relation between the intensity of the emitted radiation and the temperature of the hot body is known; secondly, recent developments in physics have revealed the fundamental character of the relation between the emission of energy by matter and the corresponding atomic processes.

In the ideal theory of temperature radiation the hot body is assumed to be of such a nature that it would absorb all radiation incident on it, whatever the nature of this radiation might be. Such a radiator, termed "a perfect black body," is rarely met with in practical pyrometry. This is a well-known fact so far as measurements of steel ingots, molten metals in crucibles and the like are concerned, but it is necessary to draw attention to the fact that

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even the radiation of closed furnaces, such as the open-hearth furnace, is not perfectly "black body." Even if, for instance, no discrepancies are noticed in the visible region of the spectrum, they do arise when infra-red radiation is taken into account, as is the case in the use of a total-radiation pyrometer.

To illustrate this point, an extreme case of departure from black-body conditions may be cited from the classical infra-red investigations of Coblenz :<sup>(1)</sup>

"It is, of course, absurd to attempt to measure the temperatures of these substances (complex minerals) with an optical pyrometer. For example, the rod of oligoclase was a perfectly transparent glass and emitted no light on heating to over 1200° C., except that due to the sparking of the platinum terminals. Nevertheless, such substances as iron oxide at the same temperature would have emitted visible light, while both emit strongly in the infra-red region."

Large discrepancies between temperatures obtained from the readings of optical and thermo-electric pyrometers led Thwing<sup>(2)</sup> to investigate the radiation of molten iron and copper. He found that the reading of a Féry total-radiation pyrometer when pointed at a molten steel surface was actually less than that obtained with the same steel when it had cooled and solidified. This was found upon examination to be due to the fact that the amount of radiation emitted by the liquid metal was only about 0·28 of that from the solid surface, which was probably covered with a coating of oxide.

Deviations from black-body radiation are known to become more noticeable with long wave-lengths of radiation. Besides these, allowance must be made for the absorption of radiation by water vapour, carbon dioxide and furnace gases and vapours.

Difficulties increase if we consider the case of hot metals outside the furnace. Here the surrounding temperature is low relative to that of the body, and consequently absorption and reflection of radiation by the hot body can usually be neglected. We can then speak of the radiative properties of the metal, or rather of the metal surface, since, except for transparent materials such as molten glasses, emissivity is essentially a surface phenomenon. Since most hot metals have surface films, oxide layers, &c., the constitution of the surface and therefore the quantity and quality of the radiation emitted are capable of great variation.

Evidently modern pyrometry is not merely a problem of instrument design, but demands an understanding of the various factors governing the radiation from the hot body. It is essential that not only the theory of this radiation be understood but that quantitative results should be available to cover so far as possible all the conditions met with in practice.

### LIST OF SYMBOLS FOR EMISSIVITY PAPER.

The following is a list of the symbols used in this paper :

- $E$  = emissivity (*see* definition).
- $E_{\lambda T}$  = emissivity at wave-length  $\lambda$  and temperature  $T$ .
- $R$  = reflectivity.
- $n$  = refractive index.
- $k$  = absorption coefficient.
- $\epsilon$  = dielectric constant.
- $\sigma$  = electrical conductivity.
- $\rho$  = electrical resistivity.
- $v$  = frequency of radiation.
- $v_r$  = resonance frequency.
- $\lambda$  = wave-length of radiation.
- $\mu$  = micron.
- $e$  = electronic charge (also used for base of natural logarithms).
- $m$  = electronic mass.
- $\gamma$  = frictional constant in electronic oscillation.
- $J_{\lambda T}$  = energy of wave-lengths  $\lambda$  to  $\lambda + \Delta\lambda$  emitted by body at temperature  $T$ .
- $C_1, C_2$  = Wien's constants.
- $T$  = temperature (in ° K.).
- $T_{app}$  = apparent temperature as measured by pyrometer.
- $S_\lambda$  = sensitivity of pyrometer to radiation of wave-length  $\lambda$ .

### DEFINITION OF EMISSIVITY.

Much confusion is caused by the various definitions and uses of the term "emissivity" that have been employed by various writers. Some use the word to signify the amount of energy in ergs radiated by each square centimetre of surface per second either normally or integrated over the whole hemisphere.

This definition is of little value unless accompanied by a very precise temperature value, since the actual energy radiated varies as a somewhat high power of the temperature of the hot body. As it is not often possible to ascertain the temperature to a high enough degree of precision, or even to maintain it sufficiently constant for the period of time involved in the making of the measurements, some alternative should be found. This is readily presented in the form of a comparison with a black body under the same conditions, and leads to the following definition of emissivity, which is certainly of greater use and significance :

If the amount of energy radiated per second per unit area by a perfect black body at a specified temperature over an infinitesimally small wave-length range be taken as unity, then the amount of energy radiated in a specified direction under the same conditions by any other body is known as the emissivity of the body.

From this definition it will be seen that the emissivity of any specified surface is a function of three variables, *viz.*, temperature, wave-length and angle of emission. If this function be integrated

over the whole wave-length range the "total emissivity" can be found. This term has been used by many writers to indicate the emissivity found by means of the so-called total-radiation pyrometer. It should, however, be pointed out that it is highly improbable that the pyrometer is uniformly sensitive over the complete wave-length range and therefore some correction\* may be necessary to allow for the characteristics of the instrument.

There are many other definitions of various types of "emissivities." Most of them are not in common use and apply only to a particular method or pyrometric device. They can all be readily calculated if the emissivity as defined above is known as a function of the three variables indicated. Worthing<sup>(3)</sup> has discussed the derivation and exact definition as well as the use of these varied terms.

In what follows, the term emissivity will, unless otherwise stated, be used as already defined.

#### BASIC THEORY.

A number of attempts have been made to explain the distribution of radiation from non-black bodies and to relate the emissivity to other physical constants.

Kirchhoff's law states that for any substance the emissivity is exactly equal to the absorptivity under the same conditions. Now the sum of the absorptivity and reflectivity under the same conditions must be unity if no energy is to be lost or gained. It follows then that the emissivity,  $E$ , and the reflectivity,  $R$ , are rigorously connected by the equation :

$$E + R = 1 * \dots \dots \dots \dots \quad (1)$$

This reduces the theory of emissivity to the theory of the optical properties of metals. Taking Drude's analysis<sup>(4)</sup> we find that the reflectivity at normal incidence can be related to the refractive index,  $n$ , and the absorption coefficient,  $k$ , by the equation :

$$R = \frac{n^2 + k^2 + 1 - 2n}{n^2 + k^2 + 1 + 2n} \dots \dots \dots \quad (2)$$

Since  $n$  and  $k$  are the basic physical constants in the optical theory of metals, this equation gives us a suitable basis for a theory of emissivity, for :

$$E = 1 - R = \frac{4n}{n^2 + k^2 + 1 + 2n} \dots \dots \dots \quad (3)$$

The next step is to reduce  $n$  and  $k$  to even more fundamental

\* On the basis of this, throughout this paper the observations of all workers have been reduced to show  $E$ , even in cases where  $R$  or other related quantities have been measured. This enables the data to be compared more readily.

quantities. This can be done by means of Maxwell's electro-magnetic theory, according to which :

$$2n^2 = \sqrt{\epsilon^2 + 4\frac{\sigma^2}{\nu^2}} + \epsilon \quad \dots \dots \dots \quad (4a)$$

$$2k^2 = \sqrt{\epsilon^2 + 4\frac{\sigma^2}{\nu^2}} - \epsilon \quad \dots \dots \dots \quad (4b)$$

for a medium of unit permeability,\* where  $\sigma$  is the electrical conductivity and  $\epsilon$  the dielectric constant of the metal, both quantities referring to a frequency  $\nu$  at which the measurements are taken.

The combination of equations (4a), (4b) and (3) gives rise to nothing essentially new, and at this stage more can be achieved by considering the various approximations that have been made, notably by Hagen and Rubens.<sup>(5)</sup>

For radiation of long wave-length, for which  $\nu$  is small :

$$\frac{4\sigma^2}{\nu^2} \gg \epsilon \quad \dots \dots \dots \quad (5)$$

Applying this to equations (4a) and (4b) we find that, as a first approximation :

$$n = k = \sqrt{\frac{\sigma}{\nu}} \gg 1 \quad \dots \dots \dots \quad (6)$$

Inserting these values in equation (3) :

$$E = 2\sqrt{\frac{\nu}{\sigma}} \quad \dots \dots \dots \quad (7)$$

If, for convenience,  $\sigma$  is replaced by  $\rho$ , the specific resistance in ohm-centimetres, and  $\nu$  is replaced by  $\lambda$ , the wave-length in microns ( $\mu$ ), then :

$$E = 36.5 \sqrt{\frac{\rho}{\lambda}} \quad \dots \dots \dots \quad (8)$$

For a higher degree of approximation, more terms must be added to equation (8), giving :

$$E = 36.5 \sqrt{\frac{\rho}{\lambda}} - 6.7 \times 10^2 \frac{\rho}{\lambda} + 9 \times 10^3 \left(\frac{\rho}{\lambda}\right)^{\frac{3}{2}} \quad \dots \quad (9)$$

The "one-term" approximation is valid for most metals for wave-lengths greater than  $10 \mu$ . Beyond this, equation (9) meets with some success up to the region of  $4 \mu$ , but eventually breaks down and in the near infra-red and the visible fails completely to give any representation of the emissivity curve.

This deviation is undoubtedly due to resonance which takes place in the electrons of the metal at these higher frequencies. The resonance of the electrons of the metal gives rise to selective

\* This is true even in the case of ferromagnetic materials, owing to the extremely high frequency of the field in the visible and infra-red portions of the electromagnetic spectrum.

emission and reflection, since both  $n$  and  $k$  will have typical dispersion curves.

According to the classical equations of the electron theory these dispersion curves may be given by :

$$n^2 - k^2 = 1 + \sum \frac{4\pi m(\nu_t^2 - \nu^2)Ne^2}{4\pi^2 m^2(\nu_t^2 - \nu^2)^2 + \gamma^2 \nu^2} \quad \dots \quad (10a)$$

$$nk = \sum \frac{Ne^2 \gamma \nu}{4\pi^2 m^2(\nu_t^2 - \nu^2) + \gamma^2 \nu^2} \quad \dots \quad (10b)$$

where  $N$  is the number of electrons of charge  $e$  and mass  $m$ , having resonance frequencies  $\nu_t$ . The frictional constant in the motion of the electrons which prevents infinite oscillations is denoted by  $\gamma$ .

The underlying theory of emissivity and the optical constants of metals has been fully discussed by Mott and Jones.<sup>(6)</sup>

Krönig<sup>(7)</sup> has applied the ideas of the quantum theory to the dispersion of light in metals. His work, resulting in complicated expressions giving  $\epsilon$  and  $\sigma$  as functions of  $\nu$ , has been tested experimentally by Hurst,<sup>(8)</sup> who found fair agreement between theoretical and observed values. There are, however, insufficient experimental data to provide a good basis for any complete theory of emissivity covering the whole wave-length range, and even less has been done to extend our knowledge of the temperature variation of emissivity with the other optical constants.

In regard to the variation of emissivity with angle of emission, it will be noted that equation (2) and its corollaries apply only to *normal* emission. A corresponding expression can be found for a general angle of emission or reflection,  $\phi$ , but at this stage it is enough to note that if  $n$  and  $k$  are known or can be determined, then an expression giving  $R$  in terms of  $n$ ,  $k$  and  $\phi$  can be found.

It is important to note that for angles other than the normal to the surface the resulting radiation will be polarised to an extent varying with the angle of incidence or emission. This portion of the theory has been tested experimentally by Laue and Martens,<sup>(9)</sup> who studied the radiation from a hot platinum strip and found good agreement with the results predicted from a knowledge of the values of  $n$  and  $k$  for this specimen.

There is a singular lack of English text-books dealing with infra-red emissivity. In their volume, "Infra-Red Analysis of Molecular Structure," Rawlins and Taylor<sup>(10)</sup> give an excellent section on the theory of infra-red vibrations within solids and liquids. Very little is, however, mentioned about the emissivity of metals, although the reflectivity of some non-metallic bodies is dealt with.

#### EMISSIVITY AND PYROMETER CORRECTION.

One of the most valuable applications of emissivity data consists in the correction of the readings of pyrometers designed for

use with black bodies, so that the true temperature of any surface can be obtained.

The type of radiation pyrometer in general use is that known as the *optical pyrometer*. It depends on the measurement of the intensity of radiation from the hot body, ideally over an infinitesimal wave-length range, but practically over a range determined by a coloured glass filter.

Wien's law, which is sufficiently true for the purpose in hand, tells us that the intensity,  $J_{\lambda T}$ , of the radiation from a body at absolute temperature  $T^{\circ}$  over an infinitesimal wave-length range centred at wave-length  $\lambda$  (in  $\mu$ ) is given by :

$$J_{\lambda T} = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \dots \dots \dots \quad (11a)$$

where  $C_1$  is a constant depending upon the arrangement of the apparatus, distance from source, &c., and  $C_2$  is a universal constant having the value 14,320 with the above units.

Now, if instead of a black body, a substance having an emissivity  $E$  be radiating :

$$J'_{\lambda T} = EC_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \dots \dots \dots \quad (11b)$$

If the pyrometer is graduated to read black-body temperatures correctly, the apparent temperature,  $T_{app.}$ , of the substance of emissivity  $E$  will be given by :

$$EC_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T_{app.}}} \dots \dots \dots \quad (12)$$

which on taking logarithms gives :

$$\frac{1}{T} - \frac{1}{T_{app.}} = \frac{\lambda}{C_2} \log_e E \dots \dots \dots \dots \dots \quad (13)$$

$$= \frac{\log_{10} E}{9,880} \text{ for a wave-length } = 0.63 \mu \text{ (this corresponding to the normal red filter)} \quad (14)$$

The last two equations may be used to correct an optical pyrometer so that it may read true temperatures, but it must be borne in mind that it has been assumed that the wave-length range used is infinitesimal.

The emissivity must, of course, be taken at the same temperature and wave-length as used above.

Attempts have been made to incorporate into equation (11b) and hence into (13) the temperature and wave-length variations of emissivity. Foote,<sup>(11)</sup> for instance, gave figures for tungsten, but his results should not be extrapolated beyond the small range given (since his formula represents only one section of the emissivity function) and have no physical significance apart from this (see Fig. 6).

The correction of other types of pyrometer can be carried out

in a similar fashion if the sensitivity curve  $S(\lambda)$  of the instrument is known. The relation between  $T$  and  $T_{app}$  then takes the form :

$$\int_{\lambda=0}^{\lambda=\infty} E_{\lambda T} S_{\lambda} \lambda^{-5} e^{-\frac{C_2}{\lambda T}} d\lambda = \int_{\lambda=0}^{\lambda=\infty} S_{\lambda} \lambda^{-5} e^{-\frac{C_2}{T_{app}}} d\lambda . . . . . (15)$$

Although this equation is somewhat forbidding it admits readily of graphical treatment.

It will be seen in the above equation that the emissivity has not been assumed constant as in equation (12), but, since a large wave-length range is used, it must be taken as a function of this variable.

#### EXPERIMENTAL TECHNIQUE.

Four main methods exist for the determination of the emissivity of metals :

(1) The pyrometer correction formula may be used in the inverse fashion. If  $T$  and  $T_{app}$  are known, then  $E$  can be calculated from equation (13). The apparent temperature may be measured by means of a total-radiation or optical pyrometer and the true temperature by means of a calibrated thermocouple or resistance thermometer.

This method may be criticised for ignoring the variation of emissivity with wave-length. For many purposes, however, this knowledge of the variation of emissivity with wave-length is not required, and therefore the procedure has been useful in obtaining empirical correction curves for pyrometric use.

It has already been pointed out above that, for a complete knowledge of emissivity, it is important that the wave-length variation be determined. The method in question does not conform to this requirement and is consequently of little use for a full investigation of emissivity problems.

(2) The emissivity of a hot body may be found by comparing its radiation with that from a standard platinum strip on which the body rests, and by means of which it is heated. This is the principle of Burgess' micropyrometer. The platinum strip and the hot body are viewed through a microscope and matched alternately with the image of a filament lamp in the eye-piece. A red filter is employed, so that monochromatic radiation is used in the comparison. Effectively the principle is that of the ordinary disappearing-filament pyrometer, except for the fact that, instead of calibrating the instrument once, with a black body, constant comparison is made with the standard platinum strip.

This technique suffers from the same defects as the previous one, since it is difficult to obtain any indication of the variation of emissivity with wave-length, and readings are necessarily restricted to the visible region of the spectrum. The micropyrometer has an effective range of 700–3000° C. and is claimed to be capable of an accuracy of 1% within this region.

(3) A direct determination of the *optical constants* of the metal under specified conditions enables the emissivity to be calculated, using equation (3). This method leads to results more fundamental than those given by a direct emissivity measurement, since  $E$  is a function of two independent variables,  $n$  and  $k$ , but is subject to the following disadvantages : (a) Present methods for the determination of the optical constants of a metal require the specimen to be prepared with a polished plane surface, which is not always a convenient procedure. (b) It is somewhat difficult to adapt the apparatus to work outside the visible region (photographic methods may be used, but in the main these are not entirely satisfactory). (c) The use of specimens at elevated temperatures demands a complicated technique.

In view of all this, unless more information is required than can be given by a direct emissivity measurement, the determination of the optical constants and subsequent calculation of  $E$  should be avoided.

(4) The remaining method which may be described as spectroscopic is conveniently discussed under two heads according as to whether it is decided to measure either reflectivity or emissivity.

Direct measurement of the emissivity presents certain advantages. Thus, should the specimen have to undergo any heat treatment crystal facets might be developed; while these would interfere with specular reflection they would not affect the emissivity, which for moderate angles is independent of direction. Then, again, since the emissivity of most metals is fairly low, the reflectivity is correspondingly high, hence a small relative error in a reflectivity measurement becomes, when transformed by equation (1), a large relative error in emissivity.

Against these advantages there is the disadvantage that for a direct determination of emissivity the radiation from the specimen should be compared with that from a black body *under identical conditions*, but as the intensity of radiation from a hot body is very sensitive to temperature variation, a small difference between the temperatures of the two bodies will produce a relatively large error in the emissivity. In view of this, no temperature difference can be tolerated, and some device must be adopted for obtaining a perfect black body under the same conditions as the specimen.

This fundamental difficulty has led many important workers, including Hagen and Rubens,<sup>(12)</sup> to fall back upon reflectivity measurements. At high temperatures reflectivity measurements are complicated by the emission of radiation from the metal under examination, but Beekman and Oudt<sup>(13)</sup> have worked out a technique for distinguishing between the reflected and the radiated energy.

In order to obtain the black body under the same conditions as the specimen for an emissivity determination, a rather ingenious principle has been used, of which there are a number of variations,

namely, that of making the black body an integral part of the specimen. Some workers have used a deep cavity or crack in a solid block of metal (Fig. 1 (a)), the surface of the metal being the specimen and the cavity or crack the black body. Others have used a strip of metal foil bent to form either a wedge of small angle (Fig. 1 (b)) (following Mendenhall and Ingersoll<sup>(14)</sup>) or a

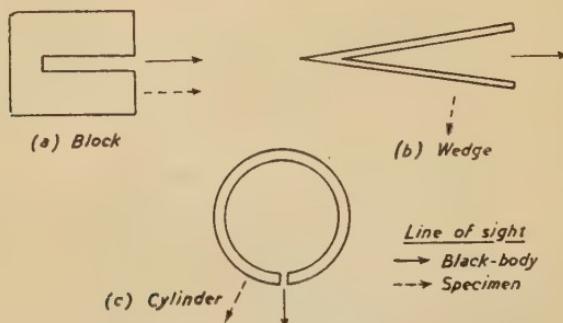


FIG. 1.—Methods for obtaining Black Body and Specimen at Same Temperature.

cylinder with a narrow gap between the two edges (Fig. 1 (c)) (following Drecq<sup>(15)</sup>).

The last two methods possess the advantage that it is easy to heat the specimen by passing an electric current down the wedge or cylinder.

In controlling the conditions of the specimen a number of points have to be borne in mind. If heat is to be applied—and we are contemplating the handling of metals at high temperatures—then special care must be taken that the surface of the metal is not contaminated. Greenslade,<sup>(16)</sup> for example, found enormous variation in the form and magnitude of the energy-distribution curves with surface purity of the specimens. Ornstein and van der Veen<sup>(17)</sup> found it necessary to use spectroscopically pure iron in their investigation of the variation of emissivity with temperature at the Curie point. It was shown that minute impurities completely destroyed a discontinuity in the emissivity-temperature graph for the pure metal.

It is obvious that for such metals as iron and copper the atmosphere must be controlled, *e.g.*, by surrounding them with an atmosphere of pure nitrogen or some chemically inert gas. In high-temperature work it is essential in addition that any refractory material used should not contaminate the metal surface and so invalidate the results.

For an investigation of the variation of emissivity with angle of emission, the geometrical configuration of the apparatus must be capable of variation. In the case of a molten metal, which neces-

sarily has a horizontal surface, the spectrometer, usually the most massive part of the apparatus, must be capable of being used in a vertical position.

Much work has been done on the spectroscopic technique needed to compare the emissivities of two radiating bodies. Indeed, in the visible region, this is normal laboratory practice in spectrophotometry. For instance, Stubbs and Prideaux,<sup>(49, 50)</sup> who made a careful investigation of the emissivity of gold, silver and copper, used a König-Wanner type of polarising spectrophotometer, details of which are given in their paper. The technique of spectrophotometry has also received much attention in the ultra-violet region, owing to its importance in the determination of chemical structure and the investigation of complex organic chemicals. The infra-red region presents most difficulties. Rawlins and Taylor<sup>(10)</sup> have described apparatus and practice. Czerny and Röder,<sup>(18)</sup> and also Matossi,<sup>(19)</sup> have recently (1938) considered progress in infra-red technique.

In view of what has been said above concerning the wavelength limitation involved in present theories, it is important to investigate the emissivity at least from the visible region up to about  $8\text{ }\mu$  to  $10\text{ }\mu$  of the infra-red region. For this purpose a quartz or rock-salt prism is necessary to produce the spectrum. To secure the requisite dispersion a quartz prism should be used for the near infra-red ( $0.7$ - $3.5\text{ }\mu$ ) and rock-salt for the far infra-red ( $3.5\text{ }\mu$  upwards).

"Fine structure" investigation demands the greater resolving power of a grating instrument constructed on the "echellette" principle as advised by Wood and Trowbridge.<sup>(20)</sup>

Probably the greatest problem in infra-red spectrometry arises from the quantitative detection of the radiation. Coblenz<sup>(21)</sup> has fully discussed the merits and demerits of the usual detectors. In agreement with him, modern practice favours a linear thermopile, mounted if possible in an evacuated enclosure. He has pointed out the inadvisability of using a sectored disc to reduce the apparent intensity of a source of radiation, because of its liability to introduce spurious anomalies.

The resonance radiometer as described by Hardy<sup>(22)</sup> has received some attention and appears to give excellent results. Owing, however, to the difficulties of the technique involved this method has not been used to any large extent.

The magnifying device most commonly employed with the thermopile is a split selenium cell, which is placed in the beam of light from the thermopile galvanometer. An auxiliary circuit and galvanometer connected to this cell are used to magnify the small deflections of the first galvanometer. This method seems to be very successful in practice, and, although it suffers from the disadvantage that the magnification and therefore the absolute intensities are not readily determined or reproducible from experiment

to experiment, it has been employed where relative readings only are required.

### PREVIOUS MEASUREMENTS OF EMISSIVITY.

Most of the existing emissivity data are defective in that substances of unspecified purity have been examined under indefinite conditions. Moreover, measurements have been made at one or two temperatures only and for one wave-length. Often the "total emissivity" has been obtained by integrating over the whole range of sensitivity covered by the observing instrument.

A typical list of emissivity values for pyrometric use is that given by Foote, Fairchild and Harrison.<sup>(23)</sup> Values of emissivity are stated for a number of metals at various approximate temperatures and for one wave-length only, *viz.*,  $0.65\text{ }\mu$ . The International Critical Tables summarise Coblenz's work,<sup>(24)</sup> which, though good, is far from being complete. Worthing,<sup>(3)</sup> summarising results from some fifteen metals, distinguishes between normal and hemispherical emissivity. Despite the defects of the tabulated data, further probing of the literature of emissivity, with a view to determining its applicability to pyrometer corrections, has brought to light some experimental facts that have been overlooked and which are extremely suggestive for future experimental investigations.

For convenience the data are divided into sections as follows :

(1) Emissivity of non-metals and observations on substances radiating under special conditions, *e.g.*, thin films, powders, oxides, &c.

(2) Emissivity of metals and alloys, (*a*) non-ferrous, (*b*) ferrous.

(1) The most important investigation in the field of non-metallic substances was made by Coblenz,<sup>(1)</sup> whose infra-red studies are regarded as classical. The best-known part of his work is that dealing with the radiation of the Nernst lamp and other heated filaments. Coblenz showed the existence of peaks and irregularities in the emission curve of the Nernst lamp, and noted that some of these peaks were not due to temperature radiation alone. In this work the effect of power input, and therefore temperature of the filament, was carefully studied, when it was found that not only did the intensity of radiation increase with temperature as expected, but the shape of the energy/wave-length curve was considerably altered.

Certain oxides, silica and other non-metallic substances have been investigated by Schmidt,<sup>(25)</sup> Skaupy and Liebmann,<sup>(26)</sup> and Schaum and Wüstenfeld.<sup>(27)</sup> In general these investigations improved on Coblenz's work, for, although the infra-red technique of the latter was unrivalled, his results have often been too com-

plex and scanty to admit of any valuable physical analysis of the data.

Burgess and Foote<sup>(28)</sup> have used the micropyrometer to investigate non-metals. Their results suffer from the same drawbacks as all work done with this instrument, as noted above.

For present purposes the most important non-metallic substances are the oxides of iron. Burgess and Foote<sup>(28)</sup> give the following figures for "iron oxide" at a wave-length of  $0.65 \mu$ :

Temperature.	° C. . .	800	882	1058
Emissivity, $E$ .	. . .	1.00	0.97	0.94

These figures are unqualified by any indication as to the exact constitution of the oxide and the state of its surface.

Paschen<sup>(29)</sup> and Kahanowiez<sup>(30)</sup> have investigated the emission characteristics of  $\text{Fe}_2\text{O}_3$ . In both cases the results are stated in the form of energy-distribution curves, from which it is difficult to obtain values of emissivity.

The effects of tarnishing and oxidation on the total emissivity of wires have been studied by Langmuir,<sup>(31)</sup> who arrived at his values by consideration of the laws of cooling of an electrically heated wire mounted in a controlled atmosphere. He found that for bright cast iron at  $300$ - $400^\circ \text{C}$ . the emissivity was 0.22. For the same metal when oxidised this figure was increased to 0.60, and over a higher temperature range to 0.62.

In much of the work on oxides and similar substances it has been found that, because the radiating body was appreciably transparent to infra-red radiation, the emissivity appeared to vary considerably with the thickness of the specimen. This is especially noticeable for small thicknesses, and will, of course, affect deductions concerning the changes of emissivity due to thin films of oxide on the surface of a metal.

Another correlated phenomenon is the influence of particle size on the emissivity of a powdered substance. This has been investigated by Pfund,<sup>(32)</sup> who showed that the radiation curves of powdered quartz were very different from that of the crystalline substance.

The emissivity of thin films of metal has been investigated by Barnes and Czerny,<sup>(33)</sup> and also by Goos,<sup>(34)</sup> who made detailed measurements on thin layers of silver. As it is impossible to heat a thin film without damaging it, the reflectivity and not the emissivity must be measured. It was found again that the reflectivity varied with the thickness of the film as well as its tarnishing and ageing and consequent structural changes. An equation relating reflectivity and thickness was derived and tested experimentally by Barnes and Czerny.<sup>(33)</sup>

(2a) It is remarkable that only a few workers have dealt at all adequately with the dependence of the emissivity of metals on temperature and wave-length. Greenslade<sup>(16)</sup> gives actual energy/

wave-length curves for a metal at one temperature only. Fragstein<sup>(35)</sup> has made reflectivity measurements over a large range of wave-lengths, extending from the ultra-violet to the near infra-red.

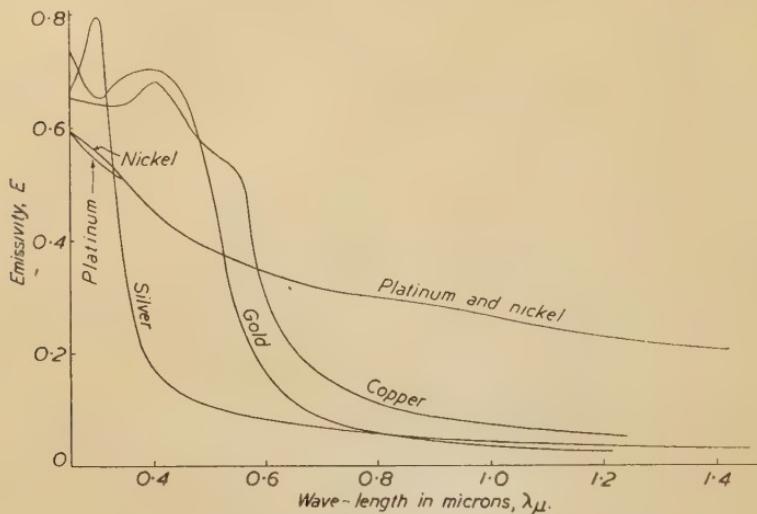


FIG. 2.—Emissivities of Metals at Room Temperature.

His temperature range, unfortunately, was limited. Hagen and Rubens<sup>(12)</sup> give numerous data on room-temperature reflectivity for silver, copper, gold, platinum and nickel, as well as for iron, in the visible region (see Fig. 2).

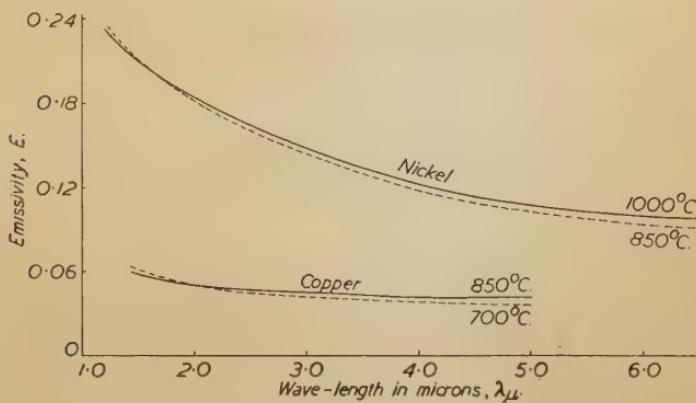


FIG. 3.—Emissivities of Copper and Nickel (Hurst<sup>(8)</sup>).

Among the best papers dealing with non-ferrous metals are those of Hurst,<sup>(8)</sup> who measured the emissivity of copper and nickel in the near infra-red region for temperatures of 700°, 850° and 1000° C. (see Fig. 3). This work is worthy of note, as some

indication is given of the variation of emissivity with angle of emission. For instance, at  $850^{\circ}$  C. and a wave-length of  $3.5\mu$  with a copper or nickel surface, it was found that, beginning with normal emission, the emissivity increased with angle, reaching a maximum of about 1.4 times normal emissivity at about  $80^{\circ}$ . For greater angles the emissivity decreases rapidly. For angles of emission less than  $20^{\circ}$  the deviation from a hemispherical even distribution is usually smaller than 1%. This variation of emissivity with angle has been explained, as noted above, in terms of the refractive index and absorption coefficient of the emitting material. Hurst checked this theory by measuring  $n$  and  $k$  for the specimen under consideration and comparing the calculated distribution with the observed phenomena. Agreement was reached qualitatively but not quantitatively.

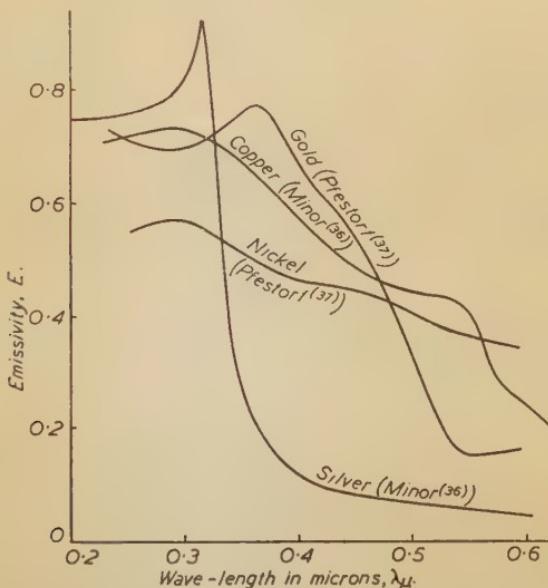


FIG. 4.—Emissivities of Nickel, Copper, Gold and Silver at Room Temperature.

The measurement of the optical constants has been used for the determination of emissivity values by Minor<sup>(36)</sup> and by Pfessorf.<sup>(37)</sup> The results of the former for copper and silver, and of the latter for gold and nickel, are shown in Fig. 4. Minor's results for iron appear in Fig. 9.

It has long been known that the radiation emitted obliquely from an incandescent solid or liquid is partially polarised in a plane perpendicular to the plane of emission and that, in consequence, the radiation originates not only from the surface molecules but also from those below. Czerny<sup>(38)</sup> actually used the

oblique radiation from a platinum strip at  $850^{\circ}$  C. as a source of completely polarised infra-red radiation.

The angular variation of emissivity has been investigated experimentally by Worthing<sup>(39)</sup> and by Spiller.<sup>(40)</sup> The former studied in detail the emissivity obtained by considering the polarised components of the emitted radiation, while the latter examined the effect of surface contamination on the variation of emissivity with angle. Both investigators worked with white-hot tungsten, radiating at a wave-length of about  $0.66 \mu$  (in the visible-red region). A comparison of results (Fig. 5) shows the large influence exerted by surface oxidation.

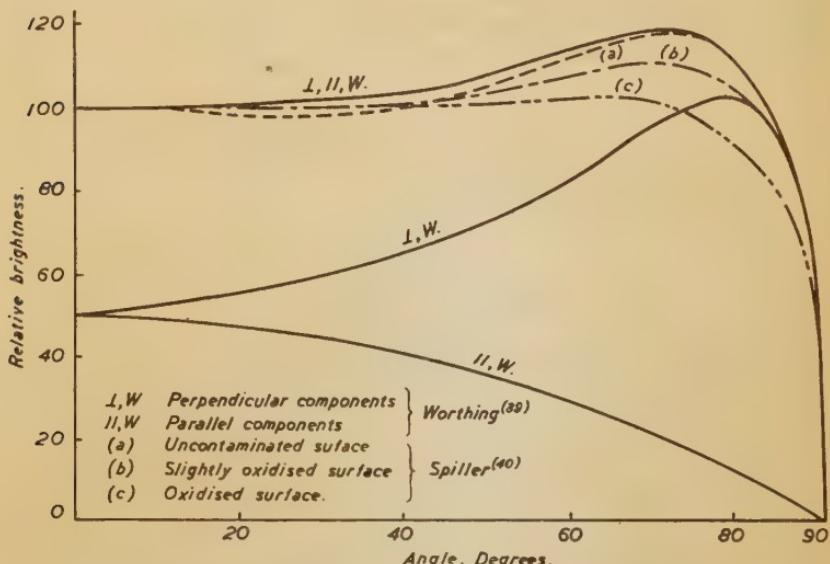


FIG. 5.—Variation of Emission with Angle (white-hot temperature,  $\lambda = 0.66 \mu$ ).

Kirchhoff<sup>(41)</sup> and also Laue and Martens<sup>(9)</sup> studied this polarisation at oblique angles theoretically, and the latter found an expression relating the degree of polarisation to the optical constants ( $n$  and  $k$ ) and the angle of incidence. If the results obtained experimentally for the degree of polarisation are compared with figures deduced from the known values of the optical constants, fair agreement is reached. Zwikker,<sup>(42)</sup> working with tungsten, found that the observed variation corresponded to an emissivity of 0.44 ( $n = 2.90-2.96$ ;  $k = 3.35-3.36$ ).

It should be noted that, because of this emission of polarised light, precautions must be taken if a polarising instrument such as the König-Wanner spectrophotometer is used. If the incident light is already polarised, the readings of the instrument are usually invalidated.

Tungsten is the only metal of which radiation constants have been thoroughly investigated, no doubt on account of its importance in the design and manufacture of electric lamps and the fact that the metal can be obtained comparatively easily in a pure state. Nyswander,<sup>(43)</sup> measuring the energy-distribution curves for heated tungsten up to a wave-length of  $6\ \mu$ , found definite minima at  $2.7\ \mu$  and  $4.3\ \mu$ . These, it is reasonable to assume, are due, not to the emissivity variation of the tungsten, but to the strong absorption bands of carbon dioxide at  $2.7\ \mu$  and  $4.4\ \mu$ .

The most detailed study of tungsten seems to be that of Ornstein,<sup>(44)</sup> who has given comprehensive tables of emissivity data extending from  $0.25\ \mu$  to  $2.0\ \mu$  and from  $1600^\circ$  to  $3000^\circ$  K. ( $1327^\circ$ - $2727^\circ$  C.). A very remarkable result that does not appear to have

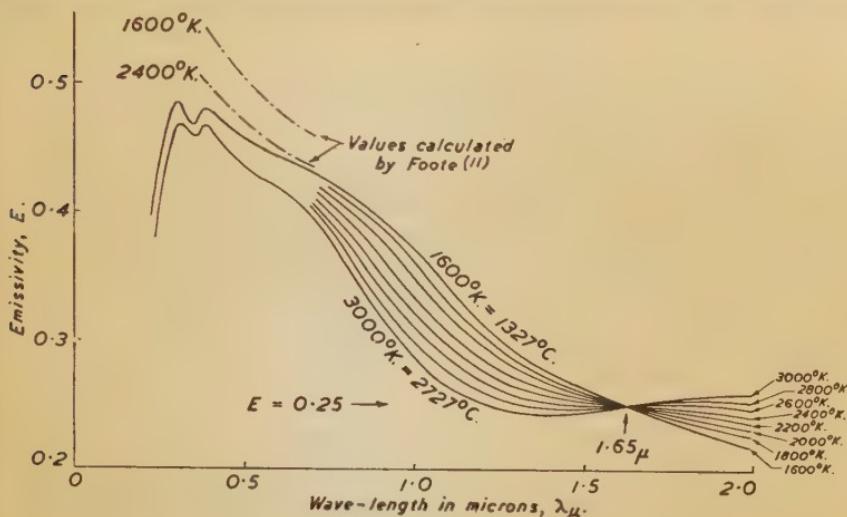


FIG. 6.—Emissivity of Tungsten.

received the attention which its novelty demands may be drawn from these data as plotted in Fig. 6. It will be noticed that all the curves are concurrent at about  $1.65\ \mu$ , or, in other words, the emissivity is the same, *viz.*, 0.25 approximately for all temperatures. This phenomenon is all the more interesting since, in spite of the absence of complete data, most metals appear to show this concurrency for some wave-length or other. Apparently no satisfactory explanation has yet been evolved. Weniger and Pfund,<sup>(45)</sup> in their investigation of the temperature coefficient of reflectivity for tungsten in the infra-red region, noted that the temperature coefficient was zero at  $1.27\ \mu$ . Forsythe and Worthing<sup>(46)</sup> give a similar series of graphs (Fig. 6) for tungsten. These again show concurrency, this time at  $1.3\ \mu$ . The discrepancy between the observations of these different workers is probably due to contaminated metal surfaces. The curve for room-temperature

emissivity of tungsten in Fig. 6 is drawn from the reflectivity measurements of Coblenz.<sup>(47)</sup> Over small ranges, Kahanowicz<sup>(30)</sup> has attempted to fit curves of the types "Energy =  $KT^n$ " to the radiation distribution of platinum, gold and other substances. Owing to the small range studied, this has little physical significance (see Fig. 6).

Platinum is another metal that has received special attention, although few data seem to exist on the wave-length, temperature and angular variations of emissivity. McCauley<sup>(48)</sup> has carried out investigations with platinum, palladium and tantalum. It was found that the dependence of reflectivity on temperature was small for all three metals in the infra-red region, but differed in the visible. There was in each case a minimum of reflectivity in the near infra-red, which became increasingly marked with temperature.

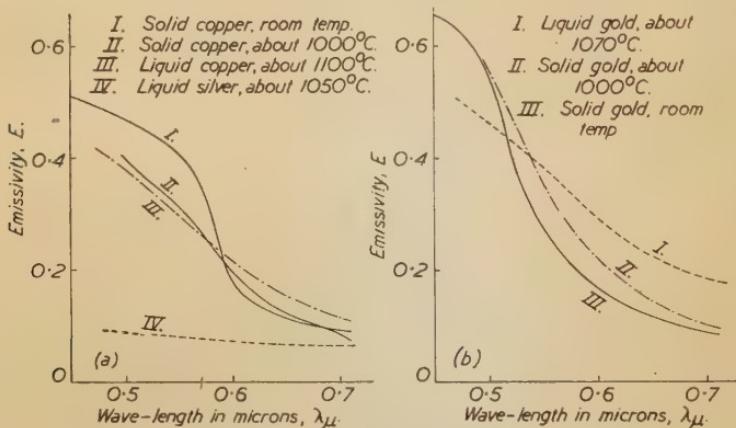


FIG. 7.—Emissivities of Copper, Silver (Stubbs<sup>(49)</sup>) and Gold (Stubbs and Prideaux<sup>(50)</sup>).

In the visible, Stubbs<sup>(49)</sup> investigated copper and silver (Fig. 7 (a)) and Stubbs and Prideaux<sup>(50)</sup> worked with gold (Fig. 7 (b)). This work is of special interest, as it is one of the few cases in which the molten metal has been studied in any detail. The authors found a sharp discontinuity in the shape of the spectral-emissivity curve at the melting point. Although such a change might be expected in accordance with similar discontinuities in other physical properties, it has been denied by many workers. This denial has been so strong that a standard of radiation has even been based on the emission from platinum at its melting point. Any discontinuity would naturally render this standard invalid. Worthing<sup>(51)</sup> also carried out observations on gold. The results indicate that for a wave-length of  $0.47 \mu$  the temperature coefficient of emissivity is zero. The measurements, however, are sparse and need confirmation.

Nickel has received special attention by Hagen and Rubens,<sup>(52)</sup> who studied the temperature variation, especially in the region at which the magnetic properties show a sudden change. Cennano<sup>(53)</sup> has also studied the temperature variation with nickel, this time above the Curie point. His results show a concurrency at a wavelength of about  $2\cdot2 \mu$ , at which the emissivity is 0.83. The reflectivity of nickel at temperatures between  $20^\circ$  and  $920^\circ$  C. has been measured by Reid<sup>(54)</sup> for wave-lengths from  $0\cdot8 \mu$  to  $11\cdot0 \mu$ . The observations were found to be in accord with equation (8) for wave-lengths greater than  $5 \mu$ . Below this the reflectivity decreased more rapidly than was indicated by the formula, and passed through a sharp minimum of 0.58 at  $1\cdot0 \mu$ . The ratio of the reflectivity at  $920^\circ$  to that at  $20^\circ$  C. changed from 0.9 at  $5 \mu$  through 1.0 at  $2\cdot15 \mu$  (point of concurrency) to 1.06 at  $0\cdot8 \mu$ . The results are qualitatively in agreement with those of Cennano.<sup>(53)</sup>

(2b) In this section a number of miscellaneous observations are noted on the emissivities of iron and various steels. Emissivity studies of iron have, no doubt, suffered from the difficulty of obtaining the metal in a pure state and free from surface activity and contamination. Values of emissivity for red light and for total radiation have been obtained by Randolph and Overholzer,<sup>(55)</sup> Burgess and Waltenburg<sup>(56)</sup> and Aschkinass.<sup>(57)</sup> These are all isolated readings and from them no general understanding can be obtained of the variation of emissivity with the conditions under which the specimen is radiating. An investigation of the variation of total emissivity with temperature has been made by Bidwell.<sup>(58)</sup> His results are of special interest, as the region studied includes

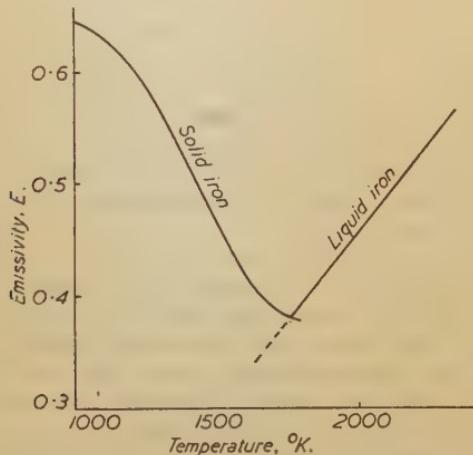


FIG. 8.—Emissivity of Iron as a Function of Temperature ( $\lambda = 0\cdot65 \mu$ ).

the melting point, hence both the solid and liquid states have been examined. The results obtained are shown in Fig. 8. The

total emissivity of iron has also been measured by Hase,<sup>(59)</sup> who verified equation (8) in the region 750–1200° C. Blaurock<sup>(60)</sup> has determined directly the optical temperatures of liquid iron and steel for a mean wave-length of 0.65  $\mu$ . Many tables of temperature corrections are given, but, on the whole, the work must be regarded as empirical. The optical constants of steel have been measured in the visible region by Pfestorf<sup>(37)</sup> and by Minor.<sup>(36)</sup> The emissivity curves calculated from these results appear for comparison in Fig. 9. In the ultra-violet region the reflectivity

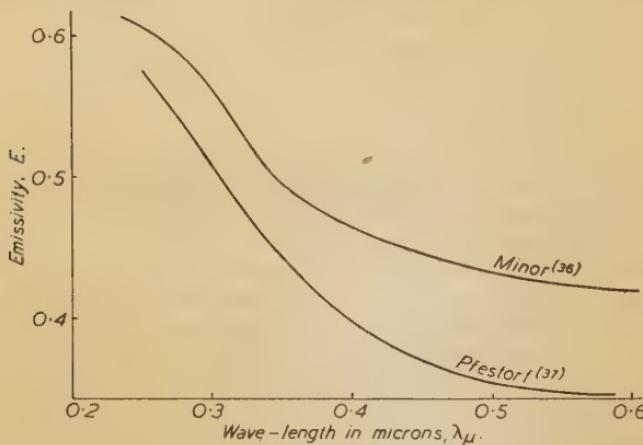


FIG. 9.—Emissivity of Steel at Room Temperature.

of steel at room temperature has been measured by Fragstein.<sup>(35)</sup> The effect of surface contamination on the spectral reflectivity in the visible region has been studied by Clavier,<sup>(61)</sup> and in the special case of thin films of iron this problem has been dealt with by Cau.<sup>(62)</sup> In the course of his infra-red researches, Coblenz<sup>(63)</sup> took observations at room temperature on the spectral reflectivity of iron up to 9  $\mu$ . His results are shown for comparison with those of Hagen and Rubens<sup>(5)</sup> in Fig. 10.

There have been only two papers dealing in any detail with the spectral distribution of radiation from heated iron. Green-slade<sup>(16)</sup> gives graphs of energy emitted by iron as a function of wave-length. Data in this form, however, as has been pointed out, have little physical significance, since the conditions of radiation, especially the temperature, are not known to a high enough degree of accuracy. The most complete paper on spectral distribution of emissivity for solid and liquid iron is due to Hase,<sup>(64)</sup> although here again it is energy and not emissivity that has been measured. The hot body was an electrically heated strip of pure iron or wrought iron in argon. In addition to this the radiation from pure liquid iron at a temperature of 1573° C. was also measured.

Observations were taken on the solid at three or four temperatures, on the liquid at one temperature and also on a comparison black body. The only data appearing in Hase's paper consist of three

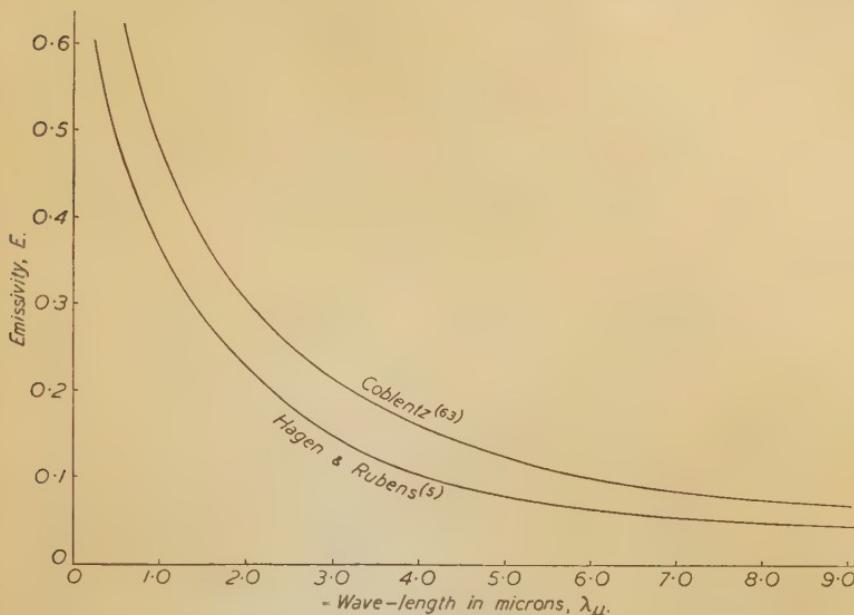


FIG. 10.—Infra-Red Emissivity of Iron at Room Temperature.

graphs, giving the spectral distribution of energy for pure iron, wrought iron, liquid iron and the black body, each at a number of temperatures and in a wave-length range from  $1 \mu$  to  $4.5 \mu$ . In addition to this there appears only a short investigation of the variation of wave-length of maximum emission with temperature. As these emission curves are the only existing data published on the infra-red spectral emissivity of solid and liquid iron, it was deemed of some importance to deduce from them, if possible, the emissivity curves. Careful measurements were made from the graphs and fresh curves were drawn of energy against temperature for all the specimens. From these curves, making the (admittedly doubtful) assumption of a negligible temperature coefficient of emissivity, the energy emitted at a temperature of  $1573^{\circ} \text{ C}$ . was found at a number of wave-lengths over the range covered. Having, now, energy distributions for wrought iron, pure iron, liquid iron and the black body at the same temperature it was possible to deduce the emissivity curves. These are shown in Fig. 11. It was found, as was to be expected in view of the incomplete state of the original data and the simplifying assumptions made in reducing them to the given form, that large deviations from a smooth curve were present. Some indication was, however, obtained of

the trend of this curve, which provides, as far as is known, the only recorded data on the infra-red emissivity of iron.

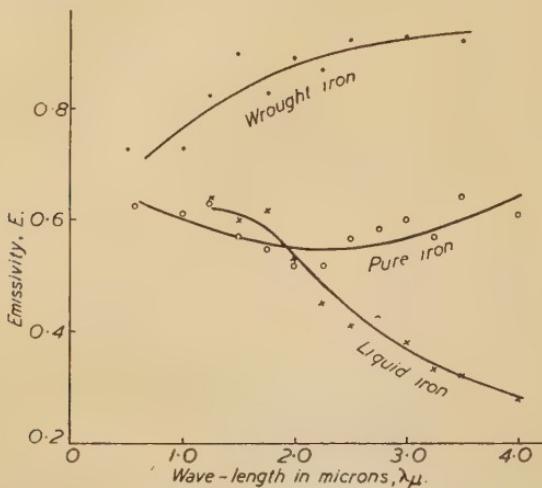


FIG. 11.—Emissivity of Iron at 1573° C. (derived from data by Hase<sup>(59)</sup>).

Ornstein and van der Veen<sup>(17)</sup> have made a study of the change in emissivity of iron with temperature, especially at the discontinuity in the region of 1200° K. Results were obtained for a number of wave-lengths in the visible (Fig. 12). The discon-

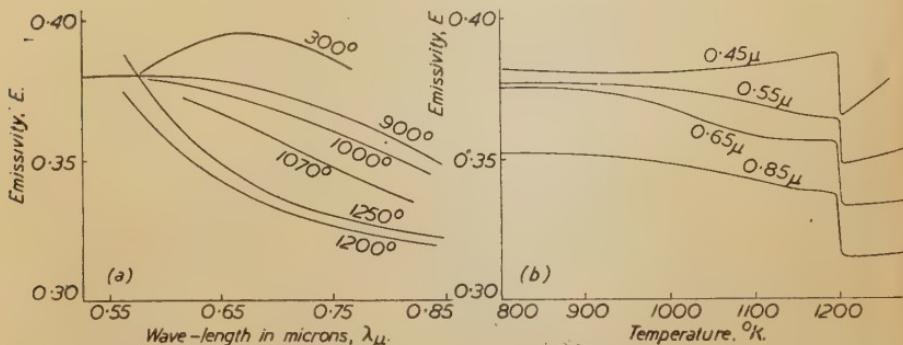


FIG. 12.—Emissivity of Pure Iron, hydrogen- and vacuum-treated, as a function of wave-length and temperature.

tinuity is only sharp if elaborate precautions are taken to ensure absolute purity of the iron surface. A small trace of contamination is sufficient to cause the break to smooth out and eventually vanish.

## CONCLUSION.

In view of the paucity of data at present available, a complete investigation of the emissivity of iron and other metals is needed. Not only should spectral emissivity be measured over a wide range of temperature, but care should be taken to investigate the variation of emissivity with angle, state of surface and purity of specimen. Experiments on these lines are now being carried out by the present authors, under the auspices of the Foundry Steel Temperature Sub-Committee of the Steel Castings Research Committee, reports of which will be published from time to time.

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# THE DRIFT OF SELENIUM PHOTO-ELECTRIC CELLS IN RELATION TO THEIR USE IN TEMPERATURE MEASUREMENT.<sup>1</sup>

BY J. A. HALL, A.R.C.S., B.Sc., D.I.C. (PHYSICS DEPARTMENT, THE NATIONAL PHYSICAL LABORATORY, TEDDINGTON).

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(submitted by the Liquid Steel Temperature Sub-Committee).*

## SUMMARY.

The paper describes experiments made to investigate the "drift" effect in selenium barrier-layer photo-electric cells intended to be used for temperature measurement. It was found that the drift of seven of the nine cells examined was too great to permit of their use for the most accurate work. However, a comparison with work done by Land showed that his cells were, on the average, more satisfactory and that, by pooling the two batches, eleven satisfactory cells could be obtained from a total of nineteen.

The following characteristics of the drift effect were noted. The drift, expressed as a percentage, is independent of the current given by the cell, and hence of the brightness to which the cell is exposed. If a cell is allowed to drift by exposure to radiation from a source at a given temperature and the temperature is then increased, the initial response to the higher temperature is almost, but not quite, as great as if the cell had not previously drifted at the lower temperature. Drift is much reduced when deep-red and infra-red radiation is excluded. Among the filters examined, a  $\frac{1}{4}$ -in. thickness of Calorex glass was sufficient to obtain the maximum observed reduction in drift (about 50%). No drift was observed when the cell was exposed on open circuit. If the illumination of a cell is interrupted for a short period and then resumed, the sensitivity of the cell recovers somewhat during the "rest" period, but rapidly resumes the value it had had just before, irrespective of whether it had previously been allowed to drift for a long or a short period. The speed of recovery depended to some extent on the circuit conditions under which the cell was allowed to recover, and was most rapid when the cell was short-circuited.

## INTRODUCTION.

WHEN work was started on an investigation into those properties of selenium barrier-layer photo-electric cells which would determine their suitability for use in high-temperature measurement, the phenomenon of "drift" at once assumed a position of importance. This effect shows itself as a change (normally a diminution) in the current given by the cell under prolonged exposure to light, and its

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magnitude in most of the nine cells available for experiment was such as to make an accurate calibration impossible, except under closely prescribed conditions. The present paper describes the experiments which were carried out in order to study the effect.

#### EXPERIMENTAL ARRANGEMENTS.

No attempt was made to secure a black-body temperature calibration of the cells. All observations were made on a tungsten-strip lamp, which was calibrated by means of a standard optical pyrometer using an effective wave-length of  $0.66\text{ }\mu$ . The error introduced by the use of this method has been discussed by Land.<sup>1</sup> The electrical circuit used is that described by Campbell and Freeth,<sup>2</sup> and is the same as was adopted by Land (Fig. 1). By this means the photo-cell can be made to supply current through any desired resistance  $R_2$ , while if  $R_1$  is sufficiently large the current drawn from the potentiometer  $P$  is not great enough to affect its calibration.

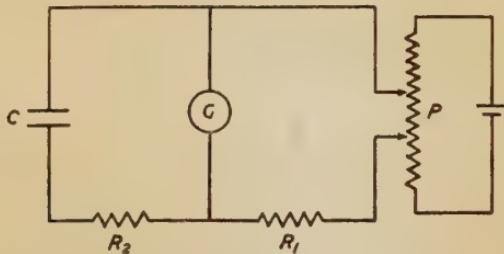


FIG. 1.—Measuring Circuit.

In the present work  $R_1$  was 10,000 ohms and  $P$  200 ohms. The error introduced by the shunting effect of  $R_1$  varies with the potentiometer setting, but in no case exceeds 0.5%. The appropriate correction was, however, applied.

The strip-lamp was a product of the Nela Research Laboratory and had a filament of about 3 mm. width. This was used in conjunction with a photographic lens of 5 in. focus and aperture  $f/3.5$  to give an image large enough to cover the photo-cell. A standard distance of 125 cm. between lens-flange and photo-cell was maintained, and under these conditions an image 25 mm. wide was formed. The full aperture of the cell (21 mm. dia.) was normally used. The same photographic lens was used with the strip-lamp when it was being calibrated against the optical pyrometer, so that the temperature calibration allowed for its absorption when the effective wave-length was  $0.66\text{ }\mu$ . Comparisons with observations made without the lens at temperatures of  $1270^\circ$  and  $1770^\circ\text{ C}$ . gave the transmission of the lens as 0.720 and 0.718, respectively.

<sup>1</sup> T. Land, "Barrier-Layer Photo-Electric Cells for Temperature Measurement," *Journal of The Iron and Steel Institute*, 1944, No. I., p. 481 p (this volume).

<sup>2</sup> *Journal of Scientific Instruments*, 1934, vol. 11, p. 125.

The cell was mounted in the centre of one face of a 9-in. hollow cube lined with black flock paper and provided with a  $2\frac{1}{2}$ -in. hole in the opposite face to admit light from the strip-lamp. By this means, and by the use of a screen round the lens, stray light was reduced to a negligible amount (less than 0.1%).

The temperature of the cells numbered 1 and 2 was measured by the use of a fine copper-constantan thermocouple soldered to the back of the cell with Wood's metal, while for the other cells a mercury thermometer was used. This thermometer was placed on top of the cube with its bulb just over the cell. While the temperatures of the cells in different experiments varied between  $17^{\circ}$  and  $21^{\circ}$  C., the temperature was maintained constant to within  $\pm 1^{\circ}$  C. throughout any one experiment. The effect of temperature is therefore presumably negligible.<sup>1</sup>

### EXPERIMENTS ON DRIFT.

Land has shown that if the cell response to brightness is linear, and  $\lambda_e$ , the mean effective wave-length, does not vary appreciably with temperature, a straight line will be obtained if the logarithm of the cell current ( $\mu$ A.) is plotted against the reciprocal of the absolute temperature ( $^{\circ}$ K.). The slope of the line is given by :

$$\frac{d(\log_{10} \mu\text{A.})}{d(10^4/{}^{\circ}\text{K.})} = - \frac{C_2 \log_{10} e}{\lambda_e} = - \frac{0.6219}{\lambda_e}$$

when  $\lambda_e$  is measured in microns and  $C_2$ , Wien's radiation constant, is  $1.432 \text{ cm.} {}^{\circ}\text{K.}$

The slope thus gives a measure of  $\lambda_e$ , which, in practice, is not very different from  $0.6219 \mu$ . The slope of the line is thus nearly  $-1$ , and hence  $\log_{10} \mu\text{A.} + 10^4/{}^{\circ}\text{K.}$  is very nearly constant. If, therefore, we plot this function against  $10^4/{}^{\circ}\text{K.}$ , we have a very sensitive indication of the magnitude and constancy of the slope of the  $\log_{10} \mu\text{A.}$  against  $10^4/{}^{\circ}\text{K.}$  curve. The curves of Figs. 2 and 3 have been plotted in this manner; broken lines show the temperature scale in degrees centigrade and the temperature changes corresponding to changes in  $\log_{10} \mu\text{A.}$  have been indicated as well as the rectangular co-ordinates.

Referring to Fig. 2, the full-line curve gives the history of the first calibration of cell No. 1, using a circuit resistance of 1000 ohms. The cell had been in the dark for more than 24 hr. at the start of the calibration, which began with an exposure to  $1063^{\circ}$  C. for 5 min., at the end of which time the cell current was measured. The strip-lamp temperature was then increased to  $1190^{\circ}$  C., and after a further 5 min. exposure the cell current was again measured. This procedure was repeated up to a maximum temperature of  $1775^{\circ}$  C., when the cell current was about  $65 \mu\text{A.}$  Observations were then taken on a falling temperature in the same manner, and a second calibration, done in exactly the same way, followed imme-

<sup>1</sup> Land, *loc. cit.*

diately. Fig. 2 shows a marked discrepancy between the first run up the range and any of the three runs (two down and one up) which followed it. These latter three do not differ among themselves by more than  $5^{\circ}$  C. at any temperature, whereas the initial run diverges by as much as  $12^{\circ}$  at  $1063^{\circ}$  C. A marked departure from linearity is shown at temperatures above  $1555^{\circ}$  C. ( $20 \mu\text{A}.$ ), but up to this point the response is as nearly linear as could be measured, the slope of the  $\log_{10} \mu\text{A.} : 10^4/\text{K.}$  curve being  $1.04$ , giving  $\lambda_e$  a value of  $0.60 \mu$ .

The other two curves in Fig. 2 were obtained in a somewhat

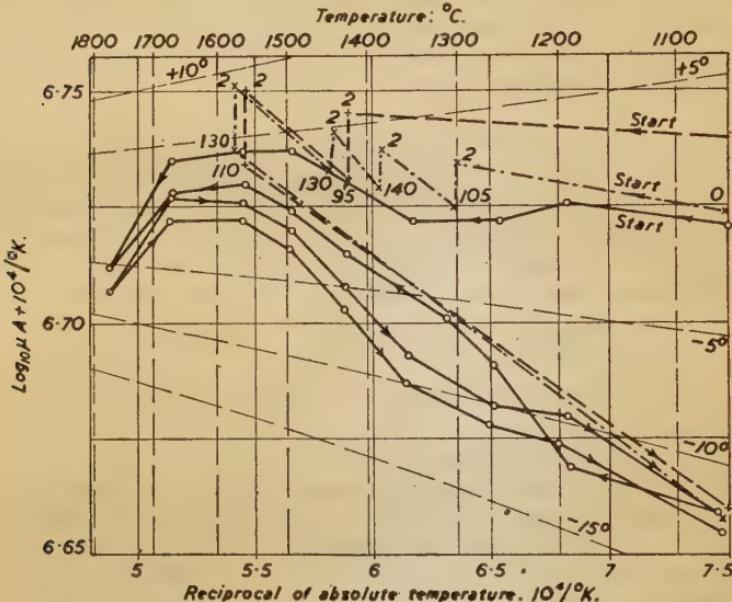


FIG. 2.—Calibrations of Cell No. 1, circuit resistance 1000 ohms.

different manner. After an initial reading at  $1063^{\circ}$  C., the strip-lamp was quickly readjusted to the first higher temperature to be observed. An observation was made after a short exposure, and regular readings were then made during the remainder of the period of exposure, which varied from 95 to 140 min. In Fig. 2 only the initial and final readings of each period have been plotted, the times of exposure in minutes being indicated by small figures adjacent to the points.

Fig. 3 shows the results of similar experiments with the same cell, but with zero external circuit resistance. It will be seen from the saw-tooth shape of the curves of both Fig. 2 and Fig. 3 that the drift effects obtained on exposures to successively higher temperatures are not fully cumulative, though, on the other hand, the broken line in Fig. 3 shows that when the temperature was increased directly

from  $1063^{\circ}$  to  $1775^{\circ}$  C. a bigger response was obtained after 1 min. exposure than when this temperature was reached after successive exposures to lower temperatures. After 140 min. exposure to

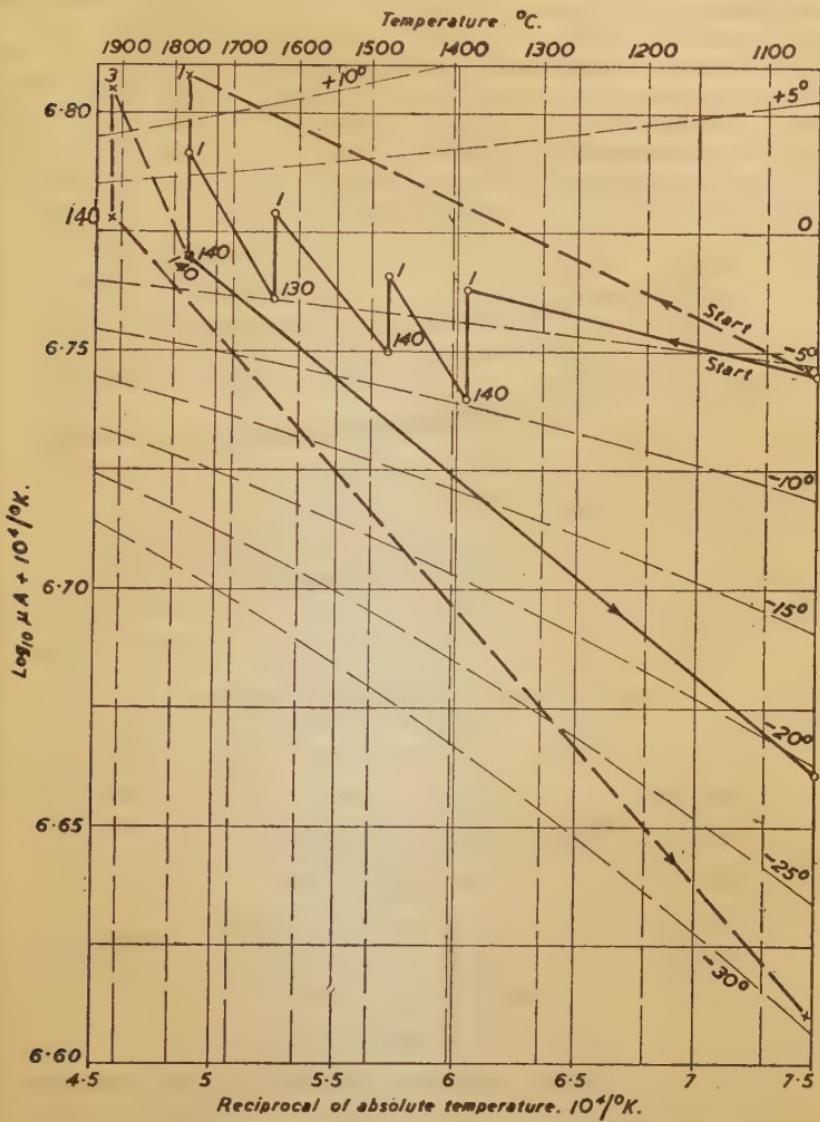


FIG. 3.—Calibrations of Cell No. 1, circuit resistance 0 ohm.

$1775^{\circ}$  C., however, the response appears to be independent of the previous history of exposure of the cell to lower brightnesses. The departure from linearity at high intensities observed in Fig. 2 does not appear in these experiments with zero circuit resistance until a

temperature of  $1775^{\circ}$  C. is reached (cell current  $80 \mu\text{A}$ . as against  $20 \mu\text{A}$ .).

Fig. 4 gives the results of a series of experiments made to compare the drifts of the nine cells in use. In each experiment the full aperture of the cell was exposed to a brightness temperature of  $1775^{\circ}$  C. under the standard conditions described above, and with an external resistance of 1000 ohms in circuit. Each cell had been kept in darkness for at least 20 hr. before exposure. A quick observation was made at  $1063^{\circ}$  C., and the cell was then covered while the temperature of the strip-lamp was adjusted. The first observation at  $1775^{\circ}$  C. was made as soon as possible (15 sec. to 1

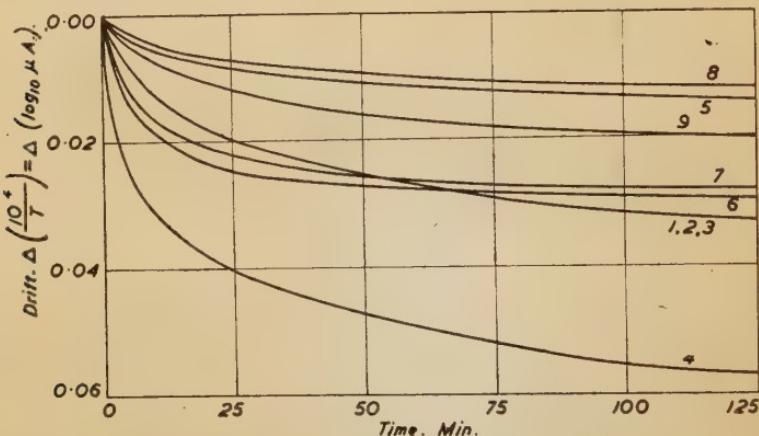


FIG. 4.—Drift Characteristics of Nine Cells.

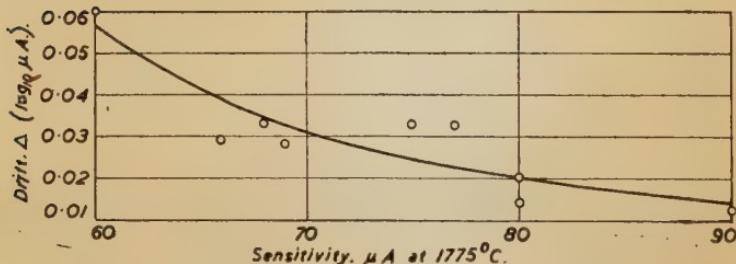


FIG. 5.—Relation between Drift and Sensitivity.

min.) after the cell was uncovered, and the biggest uncertainty in the maximum values of drift probably lies in the extrapolation back to the moment of uncovering. At any rate, the errors thus introduced would be of comparable magnitude for cells having similar drifts, so that the order of merit of the cells is not likely to be affected. It will be seen that cell No. 1, which had been used in the earlier experiments, may be regarded as typical of the bulk of the cells. Nos. 5 and 8 were markedly better and No. 4 was much

worse. In Fig. 5 the drifts given in Fig. 4 have been plotted against cell sensitivity, expressed as micro-amperes developed at 1775° C. It is clear that minimum drift is likely to be associated with maximum sensitivity.

By using the strip-lamp at different temperatures, drifts were observed with three cells at a series of current intensities. The results plotted in Fig. 6 show that, to within the limits of experimental error, the percentage drift is independent of the cell current. This result is in accordance with the experience of Land, but the

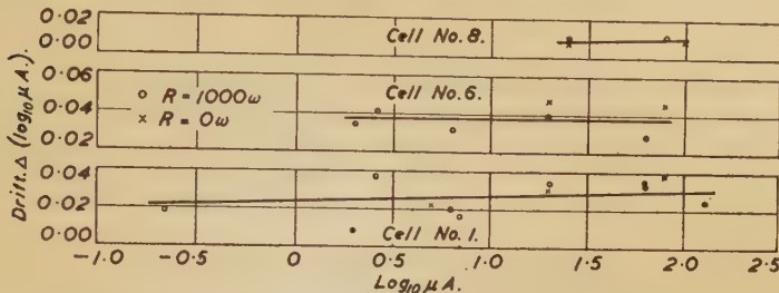


FIG. 6.—Relation between Drift and Cell Current.

average magnitude of the drifts observed was so much greater than that which he had experienced with cells of the same make ("Eel") and approximately the same date of manufacture (early 1942) that an interchange of cells was carried out.

National Physical Laboratory cells Nos. 3, 4 and 8 were sent to Sheffield and Land's cells *G*, *H* and *L* were examined at Teddington. Fig. 7 shows results obtained on cells *H* and *L* taken under conditions closely approximating to those used by Land (aperture 1 sq.

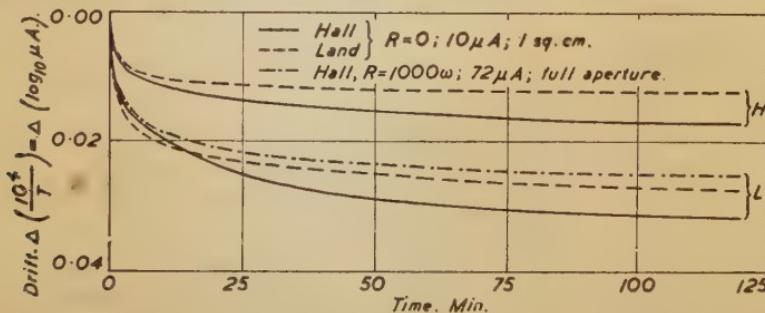


FIG. 7.—Comparison of Results on Cells *H* and *L* with those obtained by Land.

cm., cell current 10 μA.). It will be seen that drifts slightly greater than those observed by Land were obtained, the differences being probably attributable to the fact that in the present work the cells were darkened for at least 20 hr. before use, whereas Land only

darkened the cells for 30 or 40 min. Drifts of a similar order of magnitude were obtained when the full aperture of the cell was used to give a current of about  $70 \mu\text{A}$ . A typical result is shown for cell *L*. The corresponding work carried out by Land on the three typical National Physical Laboratory cells showed equally good agreement between the work in the two laboratories.

An investigation was made into the influence on drift of the spectral composition of the light employed. For this purpose the three Ilford tri-colour filters were used, but as the green and blue filters transmit about 10% and  $\frac{1}{2}\%$ , respectively, of the deep red ( $0.7 \mu$ ), a  $\frac{1}{4}$ -in. thickness of Calorex glass was used in conjunction with these to absorb the deep-red and infra-red radiation. An experiment was also made using the Calorex glass alone. Table I. gives the percentage absorption as measured by the photo-cell and the mean effective wave-length of the filters. The mean effective wave-length of  $0.66\mu$  obtained by the use of the tricolour red filter is the same as that normally employed in optical pyrometry.

TABLE I.—*Characteristics of Filters.*

Filter.	Mean Effective Wave-Length. $\mu$ .	Percentage Transmission.
Blue + Calorex . . .	0.46	2
Green + Calorex . . .	0.53	6
Red . . . .	0.66	50
Calorex . . . .	0.57	22

The results obtained are shown in Fig. 8. The final values for blue, green and Calorex alone were identical, though the drift for blue light seemed to be somewhat more rapid at the start. It is not possible to be certain of minor differences of this sort as the result of

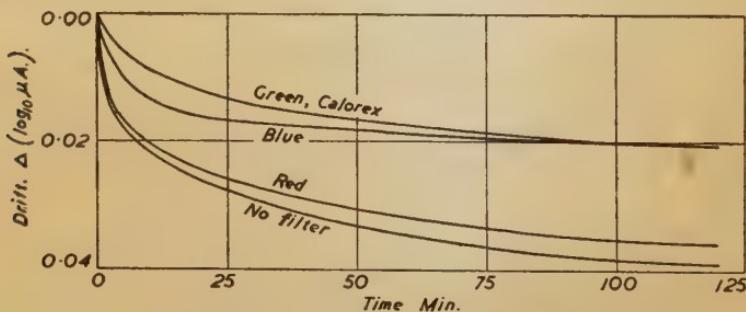


FIG. 8.—Effect of the Use of Light Filters on Drift.

a single experiment; too much depends on slight variations in the previous history of the cell. Red light and white light also gave very similar results, but showed a drift about twice as great as the shorter wave-lengths. Since the steepness of the calibration curve

varies inversely as the wave-length, the effect of a given drift on the accuracy of temperature measurement is proportional to the wavelength. The improvement effected by the use of a short wavelength is thus increased where temperature measurement is concerned.

The fact that the use of a Calorex filter alone effects as great a reduction in drift as the use of a green or even a blue filter suggests that it is only necessary to remove the deep-red and infra-red radiation in order to cut down drift to a minimum.

Cell No. 3 was exposed to  $1775^{\circ}\text{C}$ . under the standard conditions for 2 hr., but with the cell on open circuit. No drift at all was observed. On the other hand, other investigators at the National Physical Laboratory have found that if a cell of this type is set up to measure a low intensity and is then removed and exposed on open circuit for a few seconds to a high intensity (bright daylight), its sensitivity is much reduced when it is restored to its original position. Recovery, however, is very rapid.

#### EXPERIMENTS ON RECOVERY.

Recovery from the small drifts caused by exposure to the relatively low brightnesses (up to about 40 foot-candles) used in the present investigation is a slower process. Fig. 9 shows the results of an experiment carried out with cell No. 1 and a circuit resistance

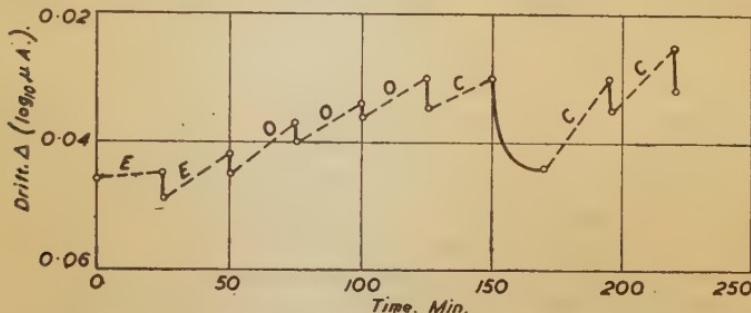


FIG. 9.—Recovery under Various Circuit Conditions.

of 1000 ohms. The cell was caused to drift by exposure to  $1775^{\circ}\text{C}$ . for 2 hr., the drop in  $\log_{10} \mu\text{A}$ . being 0.046 at the end of that time. The cell was then darkened for periods of  $24\frac{1}{2}$  min. separated by  $\frac{1}{2}$ -min. periods of exposure for observation. In Fig. 9 the broken lines indicate recovery periods and the full lines the drifts which took place during the  $\frac{1}{2}$ -min. observation periods. The start of each of these drift periods is necessarily somewhat uncertain, as automatic recording gear was not available at the time, and there was probably a lapse of some 5 sec. before the potentiometer could be re-balanced. Observations were made after recovery had taken place under three different conditions :

(1) With the cell connected to the potentiometer set to the balance-point which had been used to measure the cell current. Under these conditions an e.m.f. was applied to the cell in a direction such as to oppose the cell current had the cell been illuminated. These periods are marked *E* on the graph.

(2) With the cell on open circuit (marked *O*).

(3) With the cell short-circuited by a resistance of 1000 ohms (marked *C*).

Under condition (1) the recovery is perhaps a little slower than under condition (2), while condition (3) results in appreciably more rapid recovery. In all cases, however, the drift on re-exposure after 25 min. darkening is extremely rapid. This is further illustrated by the experiments of which the results are graphed in Fig. 10. Here, the periods of light and darkness were 4 min. and 16 min., respectively,

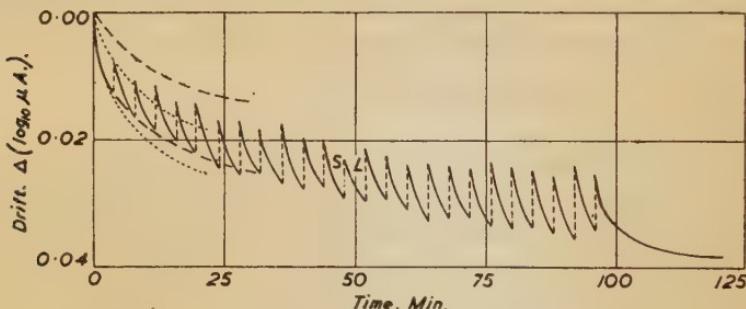


FIG. 10.—Drift under Intermittent Exposure.

and the first recovery period was started at the end of the first 4-min. exposure. The time scale of the graph only records the exposure time; the broken-line recovery periods are 16 min. each, except the two marked *S* and *L*, which were 11 and 21 min., respectively. The first observation in each drift period was made after  $\frac{1}{4}$  min. exposure and there is once again some uncertainty about the upper end of each section of the curve. It is clear, however, that the forms of all the 4-min. drifts are the same, whether they occur at the beginning or at the end of the main drift curve. This confirms the observations of rapid drifts after short recovery periods at the end of the main curve (see Fig. 9).

The curve which is plotted in full in Fig. 10 was taken with cell No. 1 working into a resistance of 1000 ohms and open-circuited for recovery. The envelopes of two other curves are also shown; they were both taken with cell No. 2, which was known to have similar drift characteristics to those of cell No. 1 (see Fig. 4). The one shown in broken lines was taken with the cell on closed circuit for recovery (condition (3)), and the one shown in dotted lines with the cell connected to the potentiometer (condition (1)). These curves confirm the conclusions drawn from Fig. 9.

## CONCLUSIONS.

The results of the foregoing experiments, taken in conjunction with the work of Land, show that if barrier-layer photo-cells are to be used for precise temperature measurement it will be necessary for them to be carefully selected. Of the nine cells used at the National Physical Laboratory, one is unusable for accurate work, six would be liable to errors of up to about  $\pm 10^\circ$  C. on account of drift alone, while with the remaining two drift would not lead to an uncertainty of more than  $\pm 5^\circ$  C. under the most unfavourable conditions. Of Land's ten cells, nine come into this last category, so that, by grouping the two consignments, eleven cells out of nineteen are satisfactory.

It appears that the best precision would be attained by calibrating the cells after exposure for a considerable time to the maximum intensity that they would experience in the pyrometer and to use them as far as possible under similar conditions. Since the cells soon return to their "drifted" condition on re-exposure after periods of darkness of half-an-hour or so, the period of exposure used in making the temperature measurement need not be long. It is probable, however, that the errors caused by drift in suitably selected cells would be small compared with those from other sources, and precautions of this kind would then be of little value.

The use of a Calorex filter would have the double advantage of reducing both the drift and the heating of the cell by radiation. It would, however, entail a considerable loss of sensitivity, and without further experience with an actual pyrometer it cannot be said whether the use of the filter would ultimately result in a gain or a loss of precision. It is probable that the use of  $\frac{1}{4}$ -in. Calorex would necessitate too sensitive (and expensive) a micro-ammeter, but possibly a useful compromise might be effected with a thinner filter.

## ACKNOWLEDGMENTS.

The work described in this paper was carried out at the National Physical Laboratory as part of the research programme of the Liquid Steel Temperature Sub-Committee and is published by permission of the Director of the Laboratory. The author wishes to acknowledge the helpful discussions that he has had with Mr. T. Land, of Messrs. William Jessop & Sons, Ltd., and the assistance that he has received from Miss V. M. Leaver, of the National Physical Laboratory, in the observational work.

[This paper was discussed jointly with the preceding four by D. Manterfield on "Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces," by T. Land on "Barrier-Layer Photo-Electric Cells for Temperature Measurement," by D. A. Oliver and T. Land on "A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures" and by D. J. Price and H. Lowery on "The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red."]

*JOINT DISCUSSION.*

The papers by D. Manterfield on "Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces," by T. Land on "Barrier-Layer Photo-Electric Cells for Temperature Measurement," by D. A. Oliver and T. Land on "A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures," by D. J. Price and H. Lowery on "The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red" and by J. A. Hall on "The Drift of Selenium Photo-Electric Cells in Relation to their Use in Temperature Measurement" were discussed jointly.

Mr. D. A. OLIVER (Director of Research, Messrs. William Jessop & Sons, Ltd., Sheffield ; Chairman of the Foundry Steel Temperature Sub-Committee), in introducing the five papers, said : The small harvest before us has been reaped from two Sub-Committees, the Liquid Steel Temperature Sub-Committee and the Foundry Steel Temperature Sub-Committee. You are already familiar with the first, under the chairmanship of Mr. W. E. Elcock, and its fine record of work.<sup>1</sup> With regard to the second, Mr. W. J. Dawson, Chairman of the Steel Castings Research Committee, suggested in July, 1941, that there was scope for corresponding temperature studies in the foundry. In April, 1942, the Sub-Committee was set up, and since then it has held nine meetings. Three of the present papers are the first-fruits of its research programme. If anyone would care to suggest any long-felt needs in this field of work the Foundry Steel Temperature Sub-Committee would be most grateful,

Referring to Mr. Manterfield's timely and excellent survey of liquid steel temperatures in basic open-hearth furnaces, his results are new, insofar that large 87-ton basic open-hearth furnaces had not previously been studied. Special problems have been overcome and full data secured. The conclusions are particularly gratifying, because, in spite of increased furnace size and extra slag burden, the variations are comparable to those encountered in the smaller furnaces previously studied by Mr. Land and myself. These are the first comprehensive figures of their kind and together with the slag-metal temperature data are significant to the determination of reaction rates in the chemistry of steelmaking. These results will be of special interest to our steelmaking friends in Canada and the United States.

Mr. J. A. HALL (Physics Department, National Physical Laboratory, Teddington) said : With reference to the selection of cells, we have made a small piece of apparatus for this purpose. It seems as though a cell can be put through a test in a matter of a couple of

<sup>1</sup> See First, Second and Third Reports of the Liquid Steel Temperature Sub-Committee, *The Iron and Steel Institute, Special Report No. 16, Section VII., 1937; Special Report No. 25, Section VII., 1939; Journal of The Iron and Steel Institute, 1942, No. I., p. 213 p.* Oliver and Land, *Journal of The Iron and Steel Institute, 1942, No. I., p. 245 p;* Barber, *ibid., 1943, No. I., p. 205 p.*

minutes or so. The circuit is simply that of Fig. 1 of my paper,<sup>1</sup> except that a second photo-cell is substituted for the potentiometer and the resistances  $R_1$  and  $R_2$  are normally omitted. The cells tend to send current through the galvanometer in opposite directions, and if their outputs are the same there is zero current through the galvanometer. We select one cell as a standard, that is, the one which has the least sensitivity and the most drift that we feel we can tolerate. We mount the two cells side by side, with an arrangement for moving one to and from a light source. If we have to move the test cell nearer to the light, it is deficient in sensitivity. If, also, we have to continue approaching it to the light to keep the galvanometer in balance, then it is drifting more than the standard and will have to be rejected. If it has to be moved in the other direction, then it is better than the standard. Since the behaviour of cells is dependent very much on their previous history, we have arranged our apparatus so that a batch of a dozen cells can be mounted together and all kept on short-circuit until they come into position to test, so that the dozen cells all have the same immediate past history as the standard. In that way we can test the dozen cells easily in half an hour.

We have also done some work on the practical application of photo-cells with instruments under works conditions, both in the melting shop and in the foundry, and, as you are aware, Mr. Land has made several instruments which he has in use. We constructed one at the National Physical Laboratory, again following in Mr. Land's footsteps. I should like to acknowledge at this stage how useful and helpful it has been to work in close touch with Mr. Land, because he has laid a good many foundations on which it has been comparatively easy to build. Our pyrometer was designed primarily for sighting on extremely small objects at considerable distances, and we have obtained results which can be described as quite encouraging. Modifications in the design of the instrument are now proceeding, and we hope that perhaps in the third or fourth model we may get something which will be really useful in works practice.

Mr. E. W. ELCOCK (English Steel Corporation, Ltd., Sheffield; Chairman of the Liquid Steel Temperature Sub-Committee) : These papers on liquid steel temperature measurement show how the work of the Foundry Steel Temperature and Liquid Steel Temperature Sub-Committees is progressing, not only in the development and application of the Schofield-Grace immersion pyrometer, but also in other branches of the main problem.

Mr. Manterfield's paper deals with the distribution of the temperature of the metal in large basic open-hearth furnaces, and gives valuable data with regard to the differences of temperature in the bath during the various stages. These results confirm the con-

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1944, No. I., p. 547 P (this volume).

clusions reached by previous investigators, even though their work was carried out on acid open-hearth and electric furnaces. The close degree of uniformity in such large furnaces is gratifying from the point of view of temperature control.

Mr. Manterfield has also given some very interesting information on the temperature of the slag, and the results obtained should prove to be extremely useful in their relationship to the temperature of the metal.

The method of Mr. Oliver and Mr. Land for measuring the temperature of a liquid steel casting stream by employing a thermocouple is an important step forward, particularly in the steel foundry. Thermocouples have previously been used for determining the temperature of the casting stream where troughs, through which the metal passes from the ladle to the ingot mould, are available. When troughs cannot be used, however, this method enables the correct temperature to be obtained, where hitherto observations have been made only with optical pyrometers. I adopted this new procedure recently, and although the length of time taken for complete casting was not great enough to ensure a steady temperature record being made, it was obvious that the method would be quite successful with castings of over 5 cwt.

Dr. Lowery and Mr. Price have provided some very interesting data on the emissivity characteristics of hot metals, with special reference to the infra-red. Their investigations so far indicate that there is a definite scope for this work. Before the introduction of the Schofield-Grace quick-immersion pyrometer the work of the Liquid Steel Temperature Sub-Committee was concerned mainly with the optical pyrometer, and it was evident that further researches were needed on the question of emissivity.

The contributions by Mr. Hall and Mr. Land on the use of photo-electric cells for temperature measurement are of considerable interest. For certain branches of high-temperature determination the employment of photo-cells would appear to offer certain advantages. The results of the experimental work carried out to date on barrier-layer cells are promising in this respect, although great care must be taken in selecting the cells.

I think it will be agreed, therefore, that these papers on the determination of high temperatures contain material which will be of interest and benefit to the steel industry.

Mr. J. S. PRESTON (National Physical Laboratory, Teddington) : My interest in the papers before us is centred mainly on the optical methods of temperature measurement and in particular on photo-electric methods, so I will restrict my remarks to the papers by Mr. Hall and Mr. Land. I think that Mr. Hall and Mr. Land have been led on by what is perhaps the most attractive and at the same time the most wayward of modern instruments. The more prim and proper emission photo-cells seem still to lead a retiring existence

in the laboratory. It is recognised, of course, that selenium rectifier cells have not so far proved satisfactory for precise laboratory work, and that this is mainly due to the fatigue or drift which they exhibit. The subject has therefore received the attention of a number of investigators, including most recently Elvegard, Lindroth and Larsson<sup>1</sup> in America and Houstoun<sup>2</sup> in Britain. In many cases the object of the experiments has been to eliminate the effect of drift in particular circumstances rather than to study the properties of the cells with a view to their improvement. Fatigue probably results from a combination of two factors, namely, changes in the electrical properties of the thin sputtered metal film on the surface of the cell and changes in the sensitive selenium layer, the latter being the more important when the photo-current is small. Fatigue is also influenced by certain external conditions such as the area of cell surface illuminated and the circuit resistance used, but these have not always been as well controlled and defined as they might have been.

In the Light Division of the National Physical Laboratory we have kept the properties of rectifier cells constantly under review, and we noticed about eighteen months ago an effect which seems to be characteristic.<sup>3</sup> We found that in certain conditions the cells showed much more fatigue for red light than for green and blue light. Moreover, the two spectral domains corresponded very closely with those for which selenium has respectively a high and a low optical transmission. (Selenium has a high transmission for red light and a very low transmission for green and blue.) One particularly interesting observation was that in the cells that we tested the effects of the two spectral regions were quite independent of each other. For instance, if we exposed the cell to red light and so produced fatigue and then changed over quickly to green light, depriving the cell entirely of red light, the sensitivity to the green was the same as that observed without previous exposure to red light. I would ask Mr. Hall whether he could confirm that result.

The other subject which interests me is the temperature coefficient of the cell. Some eight years ago we had occasion to test a large number of cells, and we found evidence of some kind of hysteresis.<sup>4</sup> Over complete temperature cycles the graph of photocurrent against temperature resembled a *B-H* curve for a ferromagnetic material. It would be interesting to know whether Mr. Hall and Mr. Land found similar effects.

In the same experiments we noticed another point concerning drift. If a cell was illuminated but the cell circuit left open, there appeared to be no drift, but the drift commenced as soon as the cell

<sup>1</sup> *Journal of the Optical Society of America*, 1938, vol. 28, p. 33.

<sup>2</sup> *Philosophical Magazine*, 1941, vol. 31, p. 498.

<sup>3</sup> Preston, *Transactions of the Illuminating Engineering Society (London)*, 1943, vol. 8, p. 136.

<sup>4</sup> Preston, *Journal of the Institution of Electrical Engineers*, 1936, vol. 79, p. 424.

circuit was closed. That did not happen with all the cells that we tested, but it certainly happened with some of them. It would be interesting to know whether Mr. Hall has any information about that, and whether, for instance, he could obtain a graph like that shown in Fig. 10 by periodically opening the circuit instead of extinguishing the light.

I think that the work described by Mr. Hall and Mr. Land indicates that there is still a great deal to be done not only in finding out more about these photo-cells but also in trying to improve them. It rather looks as though an explanation of fatigue may be found in a kind of space-charge built up slowly in the sensitive layer and depending in magnitude on the degree of penetration of the light into the layer.

The present authors have given us a much more thorough study of rectifier photo-cells than have many of their predecessors in this field and their results are correspondingly valuable. In particular, any indication of a way in which the manufacturers could improve their product would be most useful, and it is probably in studies such as these that that indication will be found. I think there is no doubt, from what has been said about the selection of good cells from a batch, that there is some feature in the manufacture which could, when once identified, be better controlled to minimise drift.

Dr. L. REEVE (Appleby-Frodingham Steel Co., Ltd., Scunthorpe) : Mr. Manterfield's paper, from the practical point of view, is probably of the greatest interest to most of those present to-day. I say that without deprecating in any way the other excellent papers under discussion ; but, whilst the methods outlined for the application of photo-electric cells to temperature measurements will, no doubt, bear fruit in the future, the method which is at present giving the most valuable results under steelworks conditions is, undoubtedly, the immersion-thermocouple method applied to liquid steel.

At Appleby-Frodingham we have applied the immersion-thermocouple method to steel furnaces of 250 and 300 tons capacity. We have not been able to investigate the distribution of temperature to anything like the same extent as Mr. Manterfield, owing to the large size of the furnaces and to the fact that we are using hand-operated thermocouples. Whilst such couples are perfectly satisfactory for the relative measurements of temperatures from cast to cast, they are possibly not as convenient as Mr. Manterfield's more elaborate arrangement for determining the distribution of temperature in the furnace. We have, however, taken temperatures at the left- and right-hand doors of a large 300-ton furnace at positions 35 ft. apart; normally, just before tap, there is not more than a 10° difference in the temperature between the extreme ends. Under special conditions larger differences may be found; for example, immediately after reversal the difference between the left- and

right-hand door of such a large furnace was on one occasion found to be  $22^{\circ}$  C. It is advisable, therefore, to take the temperature about halfway between the reversals.

A most interesting point, mentioned only briefly by Mr. Manterfield, is the relation between the temperature in the furnace and skulls in the ladle. Those familiar with tilting-furnace technique will be aware that, owing to the absence of slag on the ladles, skull formation tends to be greater than with ladles protected by a layer of slag. The actual amount of skull is a sensitive measure of the temperature of the steel. In the past skull has been used for a

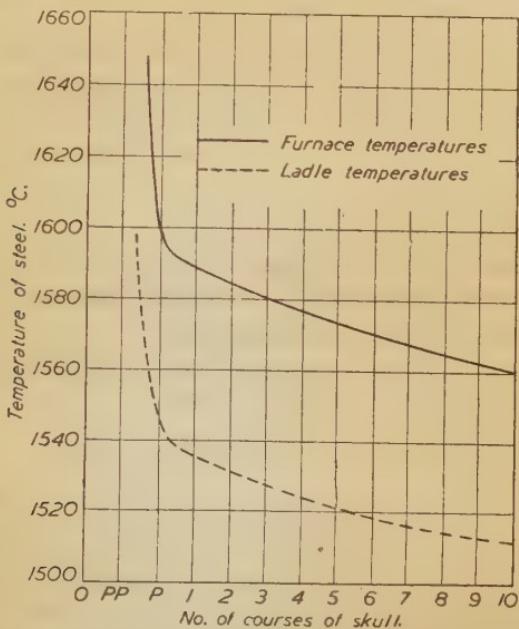


FIG. A.—Relationship between the Temperature of the Steel and the Ladle Skull. (Temperatures measured with the Schofield immersion thermocouple.)

*post mortem* review of the steel tapping temperature, and if the skull has been too heavy somebody has been blamed. The tables have now been turned, and the skull is used as a guide to the accuracy of the immersion-thermocouple reading. The sort of diagram we have found relating temperature to skull formation is shown in Fig. A, upper curve. This curve applies to steel tapping at not more than 0·20% of carbon.

The difference between a plate and a 10-course skull is only  $30^{\circ}$  C. in our experience. It means in effect that if we tap at a temperature of about  $1590^{\circ}$  C. a comparatively small drop in temperature produces a large increase in skull formation. On the other hand, if we tap very hot the skull is not so sensitive a guide, since with a fairly large change in temperature there would still be a

plate or part-plate skull at the bottom of the ladle. A summary report of temperatures taken is prepared weekly, which shows among other matters the number of readings which deviate by more than  $\pm 10^{\circ}$  C. from this curve.

In the early part of this year, over a period of some months, we took 566 immersion-thermocouple measurements at Appleby, most of which were taken 10–15 min. before tapping. Of these, 48, or 8·9%, deviated from this curve by more than  $\pm 10^{\circ}$  C. In the case of 35 measurements, some explanation could be given for the deviation; in 13 cases, or 2·3%, no explanation at all could be given apart from the hypothesis that an over-oxidised steel is sluggish and, even if hot, leaves a large skull in the ladle.

We have also taken a large number of ladle-temperature measurements and have related them to skull formation, and we have an exactly similar curve  $40\text{--}50^{\circ}$  C. below the furnace-temperature curve (Fig. A, lower curve). This figure represents the average cooling between tapping and teeming under our conditions.

I think it necessary to point out also that in practice there are quite a number of other small variables which may affect the relationship between the temperature of the steel in the furnace and the actual teeming temperature. Some of these are as follows:

- (1) Time required to fill the ladle.
- (2) Time required to empty the ladle, including the influence of nozzle size on this variable.
- (3) Age of ladle.
- (4) Quantity and nature of ladle additions.

The sum total of these factors may result in a maximum cooling effect of up to  $20^{\circ}$  C. (occasionally even more) and must be taken into account when considering the application of the immersion thermocouple to practical steelmaking conditions. It is a new tool and a very valuable one to the steelmaker, but, like all other tools, it must be used with judgment and discretion and, above all, with the co-operation of the actual steelmaking personnel.

Mr. G. T. WINCH (General Electric Company Ltd., Wembley): Speaking as one who is interested in photo-cells from the point of view of their application to photometry and allied measuring techniques, I am interested to note Mr. Hall's and Mr. Land's general confirmation of the form of characteristics of selenium rectifier photo-cells with which one is familiar.

Had I been faced with the problem of measuring furnace temperatures to the highest accuracy by photo-electric methods, I should have advocated the use of certain types of emission photo-cells, as in general an instrument of higher precision would thus be obtained. With the chosen class of emission photo-cell the fatigue would be less and the accuracy of linearity of response much greater than for the best selenium rectifier photo-cells. It is true that in the

last few years the quality of these cells has greatly improved, and if one is prepared to measure the characteristics one would expect to be able to select cells which would achieve the order of accuracy of temperature measurement indicated in Mr. Land's and Mr. Hall's papers, at least for a limited time, but this seems likely to introduce difficulties, as everyone does not possess the facilities for measuring and selecting photo-cells.

From my experience in connection with initial characteristic measurements and life tests on selenium photo-cells randomly sampled from regular manufacture over a number of years it is clear from the results that there has been a general trend towards improved performance. Concerning the particular effect referred to by Mr. Hall and Mr. Preston, namely, that these cells fatigue much more rapidly when exposed to red or white light than to blue light, I can confirm this effect, and would add that extended tests show this differential fatigue to be progressive throughout life, at least up to 300 hr. Mr. Hall has explored the effect over much shorter periods and reduces the fatigue by covering the cell with a Calorex glass filter; it would be interesting, however, to know whether the cells would still be suitable in his particular temperature-measuring application, without further correction, after extended use, in view of the progressive differential fatigue throughout life to which I have already referred.

It has been my experience with certain commercial photo-electric photometers originally equipped with emission-type photo-cells and used for measuring electric discharge lamps that, after changing over to selenium rectifier photo-cells of the most stable type in an effort to simplify the apparatus, later it has been necessary to revert to emission cells because of the errors resulting from the differential fatigue of the rectifier photo-cells.

Although there are many applications in which selenium rectifier photo-cells can be used with advantage and quite high accuracy achieved in measurements involving pure substitution techniques, where the highest accuracy is required and one is dependent on the linearity of response and stability of the photo-cell characteristics, including spectral response, at present the emission-type photo-cell is preferable.

Mr. Preston quite rightly points out that improvement in selenium rectifier photo-cell characteristics is very desirable, but, as already mentioned, steady progress in this direction is evident from the results of tests on these cells; however, suggestions for achieving further improvement would be welcomed. In the circumstances, it would seem that Mr. Land and Mr. Hall have done the right thing, namely, studied the performance of available photo-cells of the selenium rectifier type and made the best use of them, correcting for their departures from ideal characteristics.

*JOINT CORRESPONDENCE.*

Mr. T. LAND (Messrs. William Jessop & Sons, Ltd., Sheffield) wrote : The manufacture of selenium barrier-layer photo-electric cells, dealt with in Mr. Hall's paper, appears to be still at a stage where it is impossible to guarantee a consistent product. This difficulty is probably no fault of the manufacturers, but is due rather to our inexact knowledge of the effect of small quantities of impurities, which seem to have a decisive influence on the behaviour of the cells. Mr. Hall's paper shows the wide variation in fatigue properties which may be obtained from a given batch of cells, and clearly demonstrates the necessity of selecting the best cells when precision measurements are required.

The relation between drift and sensitivity which Mr. Hall has shown to hold is particularly fortunate, as it seems that the cells having the best sensitivity are also the most suitable from the point of view of drift. This should make the choice of suitable cells a relatively simple procedure.

Mr. Hall has shown that the greater part of the fatigue which occurs when white light is used is due to that part of the light which lies at the red end of the spectrum. Whilst this circumstance may prove valuable in designing pyrometers to measure the brightness temperature, its effect will have to be watched carefully if barrier-layer cells are to be used in colour pyrometers, which measure the ratio of the intensities of, say, red and green light emitted by the hot body.

The graphical presentation of the current/temperature relationship presents difficulties which I have encountered, and Mr. Hall is to be congratulated on evolving an excellent method of presentation which shows the essential features of the relationship over a wide temperature range on a comparatively small graph. Mr. Hall quite correctly implies that with this method of plotting, if the effective wave-length of the pyrometer does not vary appreciably with temperature, the calibration curve will be a straight line. It might be advisable to point out that over the wide temperature range which is covered by Mr. Hall's graphs the variation of the effective wave-length of the instrument is such that the curve for a cell of good fatigue properties is a parabola which has a minimum at about  $1150^{\circ}\text{C}$ . The ordinate at this minimum value will, of course, depend on the sensitivity of the cell, but, choosing an arbitrary value of  $6\cdot675$  for the minimum value of  $\log_{10}\mu\text{A} + 10^4/\text{K.}$ , the parabola would have ordinates of approximately  $6\cdot700$  at  $1500^{\circ}\text{C.}$ , and  $6\cdot760$  at  $1800^{\circ}\text{C.}$  In Fig. 3 of Mr. Hall's paper it will be found that the points marked 1 and the points marked 140 for the full line fall reasonably close to a pair of parabolæ of this type.

Mr. Hall mentions that the greatest errors in his measurement of the values of drift probably lie in the extrapolation back to the moment of uncovering. This is very probably true ; I found that

the drift during the first minute usually exceeded the drift during the succeeding hour. I much prefer to plot the time on a logarithmic scale, which gives a fatigue curve that is nearly straight. No question of extrapolation then arises, as drift is specified as, say, 2% between the first and the hundredth minute after exposure.

Mr. Hall has rendered a valuable service in settling the argument whether the barrier-layer cell is sufficiently stable for use in industrial pyrometry. The answer appears to be that some cells are satisfactory and others are not; the selection of suitable cells seems to be a relatively simple matter and should ensure reliable results.

I have found Mr. Manterfield's paper of particular interest. It further extends the survey of liquid steel temperatures in melting furnaces which was initiated a year or two ago, and we now have a fairly complete picture of the temperature variations which may be found in steel-melting furnaces of all types. Mr. Manterfield has opened up new fields of enquiry by developing a technique for the measurement of slag temperatures.

I have analysed the slag and metal temperature measurements which Mr. Manterfield gives in his paper with a view to estimating the temperature of the upper surface of the slag. To do this I have assumed a thickness of slag of 6 in. in each case, and I have also assumed that the temperature in the slag varies linearly with depth. Extrapolating from Mr. Manterfield's figures in this way I found that of the seven sets of observations presented, five gave slag surface temperatures in the range 1638–1646° C. This is just about the temperature at which the refractories of the roof and walls are maintained in an open-hearth furnace during the finishing stages. It would appear that during the later stages of the heat the furnace becomes a tolerably uniform temperature enclosure.

I should be interested to know whether Mr. Manterfield has any further data bearing on this point, and whether he has taken any roof temperature measurements simultaneously with the slag and metal temperatures.

Mr. A. JACKSON (Appleby-Frodingham Steel Co., Ltd., Scunthorpe), in discussion of Mr. Manterfield's paper, wrote: Several interesting papers have now been written on bath temperatures and so much work has been published that there is a great tendency to regard recorded temperatures as a final and absolute indication of tapping condition, without the necessity of qualification and in some part regardless of the art still necessary on the part of the steel melter in obtaining and retaining the conditions necessary to give an accurate and repeatable figure for the bath temperature.

Work to date indicates that accurate readings of the temperature of steel and slag can be made and that such few major errors as may occur, owing to manipulation of the instrument, are unimportant, as they can usually be detected and discarded at once by the experienced

steel man. Little trouble or loss, therefore, occurs, as a new figure can be obtained almost at once.

In brief, the instrument gives a recordable figure for something that formerly could not be recorded or repeated with certainty. When figures are quoted, however, there must be assurance that precautions were taken to ensure that they were measured under uniform conditions; otherwise there is bound to be confusion as to the precise meaning of the temperatures given by various sources, which would possibly ultimately be reflected in the scope of use of the instrument. In practice the temperatures are taken normally at a single point in the bath, and this should be a reasonably good indication of the temperatures at the ends and bottom of the bath of metal, provided that the furnace is active and boiling well; thus the skill of the melter is still necessary to see that the conditions in the furnaces are those required to make the single reading representative of the bath conditions as a whole. If this is forgotten then readings from furnace to furnace are in no way comparative. Therefore, a similar degree of operative skill is still required on the furnace with a pyrometer as with the older methods of heat testing.

The next point expected from the introduction of temperature measurement obviously is the manufacture of improved qualities of steel. This necessitates considerable knowledge of the relationship between temperature and steel defects, whether surface or internal, and the possibilities of cleaner steel. Hand in hand with this go costs, which means that the temperature must never be taken higher than is necessitated by quality considerations, dressing costs, refractories, &c. Thus the economic temperature ranges for all classes of steel must be found and used.

Deep-bath furnaces tapping several ladles offer something of a problem, and as the difference between first and last ladles may be upwards of 25° C. any safety factor on the first ladle to avoid a cold tap may give a last ladle which is too hot.

At the Appleby melting shop bogie couples of similar type to those mentioned were first tried for general service. Difficulties arose in manipulation, owing to the charger rails, and in storage when not in use. Apparatus was next designed to be inserted by the charging machine, but handling again was the difficulty. Finally hand couples of similar length and weight to a long sampling spoon were designed, and these proved easily the best for routine estimations.

For the first few months the temperatures were taken at "going on"<sup>1</sup> and no efforts made to control the tapping temperature. These results were studied and now tentative figures are available and in use for various classes of steel. There are numerous anomalies yet to be investigated, as examination of the figures in Table A will show. For purposes of investigation and correlation with former practice the temperature figures are primarily compared with the number of courses of skull on the first ladle from each tap.

<sup>1</sup> That is, at the commencement of tapping.

TABLE A.—*Skull Formation at Different Tapping Temperatures.*

Courses of Skull in Ladle.	Tapping Temperatures (going on). ° C.					
	1555–1570.	1571–1580.	1581–1590.	1591–1600.	1601–1610.	Over 1610.
Nil	...	...	...	2	...	3
PP *	...	...	...	3	5	4
P *	...	8	51	70	60	51
1	4	17	35	33	14	3
2	3	15	23	20	5	1
3	3	16	26	7	5	2
4	2	12	21	6	3	...
5	2	14	12	3	...	...
6	9	20	13	2	...	...
7	2	8	6	2	...	...
8	6	7	5	1	...	...
9	7	3	2	...	...	...
10	5	3	1	...	...	...

\* PP = Part plate. P = Plate of skull on ladle bottom.

Later the skulls on the second and subsequent ladles are compared and finally the effect of slag cover on the ladle at tapping is noted. (Only about 5% of all ladles tapped at this plant have a slag cover during teeming, an important point when comparing with fixed-furnace practice.) Only ordinary plate steels of 0·11–0·20% carbon and 0·45–0·65% manganese are noted in Table A.

One course of ladle skull or less is considered satisfactory practice, and to attain this in 90% of first ladles a temperature of 1602° C. is indicated from a graph based on Table B. Table A, however,

TABLE B.—*Proportions of Temperature Groups in Table A with One Course of Ladle Skull or Less.*

Temperature group. ° C.	1555–1570.	1571–1580.	1581–1590.	1591–1600.	1601–1610.	Over 1610.
Proportion. %	Avg. 1566. 9·3	20·3	44·1	72·4	96·7	Avg. 1617. 95·3

shows a very wide scatter, especially in the temperature groups below 1600° C., and obviously there is still very much work to be done to discover why, say, in the 1581–1590° C. groups 44% of the ladles have less than one course of skull whilst some 14% have from six to ten courses (a ten-course skull is the full height of the ladle). A simple answer, of course, appears to be to suggest tapping above 1600° C., but, as will be seen later, considerable production losses may result from consistently tapping at this higher temperature.

In a tilting furnace with a bath depth of some 40–42 in. the first ladle from the bottom of the furnace is definitely cooler than the temperatures shown in Table A, which are, of course, from the hottest part of the bath. As temperatures are not available for the lower

layers of the bath in normal circumstances, figures are given below for the relative skulls on the various ladles and also for the skull on ladles which had a slag cover (comprising some 5% of the whole); the figures are taken from several hundred taps just before commencing to use the thermocouple :

	1st Ladle.	2nd Ladle.	3rd Ladle.	Slag Cover on 3rd Ladle.
Percentage of each group with one course of ladle skull and less .	48.3%	69.8%	82.2%	98.4%

The effect of slag cover is very notable, and when it inadvertently occurs on the second ladle the proportionate effect is still greater. Regarding the normal variation from first to third ladle, if all taps commenced at 1600° C. the first ladle would have very little skull, whilst the third would certainly be hotter than would be necessary to clear the ladle even without slag cover. From these figures several queries emerge :

(1) If 1600° C. is hot enough to give only a small skull in a furnace 42 in. deep, is there any advantage in tapping at a higher temperature in a fixed furnace with a more shallow bath and slag cover on the ladle ?

(2) What are the causes of the wide scatter in ladle skull over short temperature ranges ?

(3) What is the relationship between steel quality, as measured by defective ingots, and tapping temperature ?

Until these questions are fully answered there is no object in tapping above the minimum permissible temperature, and if the pyrometer will enable this to be done accurately economic benefits must result. The effect of tapping temperature on furnace life is well demonstrated by an investigation made on a particular furnace which for many months was producing a type of steel at a temperature about 25–30° C. above that necessary for ordinary section steels; the mean weekly production was reduced by over 15% and the annual production by over 20%, the latter being due to more frequent repairs. The production loss was due partly to waiting for the extra temperature at tapping, but to a greater extent due to the extra fettling involved and the increased time necessary to burn this in.

Finally, what is considered to be the controlling temperature of tapping ? Is it the temperature of the steel entering the moulds and chosen to avoid surface defects or is it the maximum obtained in the furnace ? If two steels are tapped at 1600° C., but one has been heated to this temperature and tapped at once whilst the other has been to, say, 1630° C. and cooled in the furnace, are the final properties in the finished material likely to be exactly the same ?

The obvious conclusion is that, whilst the taking of accurate temperatures of molten steel baths is a very big step forward, its effects on steel quality and costs must be very carefully followed up to enable full advantage to be taken of the work already done.

Dr. F. H. SCHOFIELD (Freshwater, Isle of Wight) wrote: Mr. Land's paper seems to systematise and extend our knowledge of the barrier-layer photo-cell in a manner which cannot fail to be of value to anyone concerned with the pyrometric or similar application of this instrument. The following comments are offered on the theory developed in Part I. This, as Mr. Land has indicated, follows the standard treatment of optical pyrometry and results in expressions which are mathematically correct but involve laborious calculation, as, for example, of the integrals in equation (2). If, however, the several functions of  $\lambda$  under the integral sign could be expressed in algebraic forms (even though only approximately) such that their product was readily integrable, the resulting simplification of treatment might be worth while, at any rate in the early stages of development of this subject.

It is well known, of course, that the Wien expression is readily integrable, yielding between the limits of 0 and  $\infty$  the simple form of the Stefan-Boltzmann law. Further, it will be found that products of a number of functions of the Wien type yield a single expression of this type and hence on integration between the limits named an equally simple form. The possibility of an approximate algebraic treatment is therefore opened up, provided that the functions  $\tau$  and  $S$  are expressible in Wien form. As long ago as 1905, Goldhammer<sup>1</sup> pointed out that the visibility function  $V$  was so expressible, and it may turn out that  $S$  can be similarly dealt with. In the case of the optical pyrometer a highly selective filter is almost invariably used and the resulting difficulty in getting  $\tau$  in the required form would probably make it unprofitable to pursue algebraic treatment. This would not apply to a photo-cell when used without a filter, in which case  $\tau$  would be constant, or nearly so, and consequently the method might turn out to be useful.

In carrying out the above plan we suppose that the sensitivity curve is given by :

$$S_\lambda = \lambda^{-p} e^{-q/\lambda} \quad \dots \quad \dots \quad \dots \quad \dots \quad (a)$$

This we call a Wien-type expression, since it gives the Wien form with  $p = 5$  and  $q = C_2/T$ .

In practice  $p$  will always be so large that the nearest integer gives sufficient accuracy, in which case :

$$\int_0^\infty S_\lambda d\lambda = [p - 2(q)^{-p+1}] \quad \dots \quad \dots \quad \dots \quad \dots \quad (b)$$

and similarly for the products of two or more expressions like (a). Further, we have the following relations affecting the co-ordinates ( $\lambda_m, S_m$ ) of the peak of the curve :

$$\lambda_m = q/p \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (c)$$

$$\log_{10} \left( \frac{S}{S_m} \right) = -p \left( \log_{10} \frac{\lambda}{\lambda_m} + \frac{\lambda_m - \lambda}{\lambda} \log_{10} e \right) \quad \dots \quad \dots \quad \dots \quad (d)$$

Equations (c) and (d) enable us to attempt a match of the sensitivity curve. Thus, from (d) we can get the value of  $p$  giving the closest

<sup>1</sup> *Annalen der Physik*, 1905, vol. 16, p. 621.

approximation of the ratio  $S/S_m$  at a number of chosen wave-lengths, after which we obtain  $q$  from the known value of  $\lambda_m$ .

The method outlined may be given a trial on the visibility curve and the established relation of candle-power and temperature of a black body. Here  $\lambda_m$  is  $0.555\mu$  and we select  $p = 173$ , and correspondingly  $q = 96$ . This value yields the comparison given in Table C. This represents perhaps as good a match as can be obtained

TABLE C.—Ratio  $V/V_m$  for Various Wave-Lengths.

Wave-Length. $\mu$ .	Ratio $V/V_m$ .		
	From Equation (d).	Mean Eye.*	"Red" Eye.†
0.66	0.09	0.06	0.12
0.64	0.19	0.18	0.32
0.61	0.47	0.50	0.73
0.58	0.85	0.87	0.94
0.555	1.00	1.00	1.00
0.53	0.83	0.86	...
0.51	0.53	0.50	...
0.49	0.25	0.21	...
0.46	0.04	0.06	...

\* Values adopted by international agreement.

† Values for red-sensitive eye.

by this method, and it is interesting to see what relation it yields for the brightness  $B_T$  of a black body and its absolute temperature  $T$ . We are only concerned with relative values and consequently may write from equation (b) :

$$B_T \propto \int_0^\infty \lambda^{-178} e^{-\frac{1}{\lambda}(96 + C_2/T)} d\lambda \quad \dots \quad (e)$$

$$\propto (96 + C_2/T)^{-177},$$

whence :

$$\begin{aligned} \log_e B_T &= \text{constant} - 177 \log_e (1 + C_2/96T) \\ &= \text{constant} - 177 \left[ \frac{C_2}{96T} - \frac{1}{2} \left( \frac{C_2}{96T} \right)^2 + \dots \right], \end{aligned} \quad \dots \quad (f)$$

which is highly convergent even for the lowest values of  $T$ . This expression seems to agree in form with that of Pirani and Miethling, mentioned by Mr. Land, and also with that of Fabry, who states that in addition to the term involving  $1/T$ , one with  $1/T^2$  is required at low temperatures. According to Ribaud,<sup>1</sup> the following represents the experimental results :

$$\log_{10} B_T = 7.092 - 1.0896 \frac{10^4}{T}.$$

<sup>1</sup> G. Ribaud, "Traité de Pyrométrie Optique," p. 62. (Encyclopédie Photométrique, Fifth Section, No. IV.) Paris, 1931 : Revue d'Optique théoretique et instrumentale.

Pirani's coefficient in the steel region ( $1900^{\circ}$  K.) seems to be 1.07, while equation (f) above gives for the single term :

$$\log_{10} B_T = \text{constant} - 1.10 \frac{10^4}{T}.$$

The agreement, in form and coefficient value, suggests that it may be worth while trying a similar method on the photo-cell. If the plan were feasible the limiting effective wave-length for any temperature  $T$  could readily be obtained from Foote's formula :

$$\lambda_{0(T)} = \frac{\int_0^\infty S_\lambda J_\lambda d\lambda}{\int_0^\infty (S_\lambda J_\lambda / \lambda) d\lambda},$$

which, in terms of our notation, seems to reduce to :

$$\lambda_{0(T)} = \left( \lambda_m + \frac{C_2}{pT} \right) / \left( 1 + \frac{4}{p} \right).$$

Incidentally it may be remarked that, since the limiting effective wave-length changes but slightly with temperature, the effective wave-length over a finite temperature range—see Mr. Land's equation (2)—will normally be given with sufficient accuracy by taking it as the limiting value for the mean temperature of the range.

So far we have considered only the case of black-body radiation. A precisely similar treatment would apply to tungsten radiation if we were to replace the Wien ordinate of true temperature by the Wien ordinate for the *colour temperature* of the tungsten, multiplied by the known colour emissivity  $E_c$  for tungsten and by a factor representing the change of  $E_c$  with temperature. In a similar way, if the transmission  $\tau$  of the glass envelope and optical system were not neutral but varied in a linear way with  $\lambda$ , it could be multiplied by a factor  $(1 + \alpha\lambda)$  and the resulting integration would then yield two terms instead of one.

It will be understood that the plan outlined above depends on the possibility of obtaining a satisfactory match of the sensitivity curve by means of the expression (a) embodying a single parameter  $p$ , for  $q$  is not independent, since its value is always  $p\lambda_m$ . A perfect match is, of course, out of the question, but it must be remembered that all parts of the curve are not of equal importance in this respect. Thus, for all terrestrial temperatures, the part from the peak of the curve in the direction of the longer wave-lengths is obviously of more importance than that in the other direction.

Further, even if the single expression (a) is found wanting, the possibilities of the method may not be exhausted. At first sight a building up of the curve by several such expressions covering different sections might seem to be feasible, but the resulting integration between finite limits would be altogether too cumbersome. For example, the integration of expression (e) for one finite limit

would run to some 170 terms, as against the 20 or so terms which would suffice for a satisfactory integration by Simpson's rule. Other possibilities are the adding together of two expressions of the type (*a*) with slightly displaced maxima, and the independent matching of the two parts of the curve on each side of the maximum. The latter is based on the fact that an integration between 0 or  $\infty$  and the peak of the curve appears to assume a moderately simple form in relation to the variable *T*, though not one as compact as equation (*b*). If this is correct, the device of displaced maxima could also be used. However, these possibilities have not yet been explored.

Finally, it may be remarked that the adequacy of any algebraic representation of a sensitivity curve must be judged in relation to the accuracy with which the curve itself is known. In the case of the eye, the mean curve is perhaps good to the last figure shown in the third column of Table C, but wide departures occur between individual eyes, apart from those showing definite colour blindness. To illustrate this, the values for a red-sensitive eye are given in the last column of the Table. Coming to the photo-cell, the mean curves are not known so well as for the eye. With carefully controlled manufacture, one might expect the individual departures to be less, though, in the writer's experience, marked differences in response and fatigue in the different colours suggest that at present this may not be the case.

Mr. W. M. BARRATT (Earlsdon, Coventry) wrote : I am interested in Messrs. Oliver and Land's paper on "A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures," and any information that the authors can give on the following queries will be appreciated :

- (1) Ignoring mechanical damage, what was the life of a single thermocouple ?
- (2) After the tests, were any chemical and/or spectrographical tests made on the elements ?
- (3) Did the alloy wire show any dark coating on its surface where it was in a temperature gradient of  $400^{\circ}$  to  $600^{\circ}$  C. ?
- (4) Was any test made for inhomogeneity ?
- (5) Was the temperature gradient checked along the length of sheath or was the temperature of the "head" taken ?
- (6) Were there any signs of embrittlement of the wires ?
- (7) Was any information obtained about grain-size increase and grain-boundary enlargement of the elements ?
- (8) Was the thermocouple length measured to compare it with the length of sheath?—the  $\frac{3}{4}$ -in. immersion mentioned obviously applied to the sheath. The importance of this is that, on the one hand, the tip should not touch the sheath and, on the other, the distance between the sheath and "tip" may be anything.

(9) What was the rhodium content—10 or 13%?

(10) In the case of the broken sheath, was the same element used again or a new one substituted?

(11) What was the length of the silica insulators and were there any signs, after use, of attack on the wires between the ends of the insulators?

(12) Did the sheaths show any signs of devitrification causing crystallisation with consequent loss of mechanical strength and becoming permeable to gases?

(13) Was there any sign of softening—as distinct from fusing—of the silica after subjection to the high temperature?

Some of this information would be of value to the trade, and if the authors have no data would they consider obtaining the information and publishing it?

The surprising thing to me is the high temperatures at which the rare metals were used in the presence of fused silica without any apparent attack on them, which would have quickly shown itself by altered e.m.f. characteristics had it occurred.

Mr. C. R. BARBER (National Physical Laboratory, Teddington) wrote : Mr. Land's paper has set out very clearly the basic principles of the photo-electric pyrometer employing the barrier-layer cell and has shown that, provided that precautions are taken in the selection of cells, a reasonable degree of accuracy may be attained. This, however, does not appear to equal that of a good disappearing-filament optical pyrometer. The main advantage of the type of pyrometer described over the disappearing-filament optical pyrometer would appear to be its suitability for conversion to a recording pyrometer.

I would make the following comments with regard to the theory of the instrument given by Mr. Land, which deals mainly with the two problems : (1) The calculation of the effective wave-length to be ascribed to the pyrometer, and (2) the deduction of the black-body calibration from the tungsten-strip calibration.

In order to make the second calculation it is necessary to know the effective wave-length of the system as given by the first. Mr. Land deduced the effective wave-length from the slope of the curve showing the relation between the logarithm of the cell current and the reciprocal of the absolute black-body temperature, and thus a method of successive approximations was necessary. The effective wave-length can, however, be calculated directly from the tungsten-strip-lamp calibration in the following manner.

The ratio of energy emitted by a radiator at black-body temperatures  $T'$  and  $T''$  for a wave-length  $\lambda$  is given by :

$$\frac{J'}{J''} = \frac{e - \sigma_s/\lambda T'}{e - \sigma_s/\lambda T''} = \frac{E_o' e - \sigma_s/\lambda T_o'}{E_o'' e - \sigma_s/\lambda T_o''}$$

where  $T'_c$  and  $T''_c$  are the colour temperatures corresponding to the brightness temperatures  $T'$  and  $T''$  and  $E'_c$  and  $E''_c$  are the colour emissivities at the two temperatures. Therefore :

$$\log \frac{J'}{J''} = \frac{C_2}{\lambda} \left( \frac{1}{T''_c} - \frac{1}{T'_c} \right) + \log \frac{E'_c}{E''_c}.$$

Taking into account the deviation from linear response as given by Mr. Land (equation (5)) :

$$\lambda = \frac{C_2 \left( \frac{1}{T''_c} - \frac{1}{T'_c} \right)}{\frac{1}{b} \log \frac{i'}{i''} - \log \frac{E'_c}{E''_c}}.$$

Substituting values of  $E_c$  and  $T_c$ <sup>1</sup> for tungsten and Mr. Land's values of  $\log i$  from Table VIII(B). in the above expression we obtain mean values of  $\lambda$  for temperature intervals 1275–1325°, 1475–1525° and 1675–1725° C. of 0.608, 0.604 and 0.597, respectively, showing close agreement with those set out in Table VII.

The difference between the black-body and tungsten-strip calibrations of the photo-cell pyrometer arises from the difference of effective wave-length of the photo-cell from that of the optical pyrometer employed in the calibration of the tungsten-strip lamp. Thus, if we correct this calibration to be valid for the photo-cell pyrometer wave-length then the temperatures given will be black-body temperatures.

We have for the ratio of energies at two wave-lengths  $\lambda_1$  and  $\lambda_2$  :

$$\frac{J^1}{J_2} = \frac{\lambda_1^5 e^{-C_2/\lambda_1 T_1}}{\lambda_2^5 e^{-C_2/\lambda_2 T_2}} = \frac{\lambda_1^5 e^{-C_2/\lambda_1 T_0}}{\lambda_2^5 e^{-C_2/\lambda_2 T_0}},$$

where  $T_1$  and  $T_2$  are the black-body temperatures corresponding to  $\lambda_1$  and  $\lambda_2$ . Hence :

$$\begin{aligned} \frac{1}{\lambda_2 T_2} - \frac{1}{\lambda_1 T_1} &= \frac{1}{\lambda_2 T_c} - \frac{1}{\lambda_1 T_c} \\ \therefore \frac{1}{T_2} &= \frac{\lambda_2 - \lambda_1}{\lambda_1} \left( \frac{1}{T_1} - \frac{1}{T_c} \right) + \frac{1}{T_1}. \end{aligned}$$

For black-body temperatures ( $\lambda = 0.66\mu$ ) of 1300°, 1500° and 1700° C. we obtain from the above expression corresponding values of 1309°, 1512° and 1718° C. for  $\lambda = 0.608$ , 0.604 and 0.597, respectively, as calculated above. The difference between these two sets of temperatures will be seen to agree almost exactly with the difference between the black-body and tungsten-strip calibrations given in Table VIII.

<sup>1</sup> G. Ribaud, "Traité de Pyrométrie Optique," p. 448. (Encyclopédie Photométrique, Fifth Section, No. IV.) Paris, 1931 : Revue d'Optique théoretique et instrumentale.

*AUTHORS' REPLIES.*

Mr. MANTERFIELD wrote in reply : It is very gratifying to find that so much interest has been taken in this question of liquid steel temperatures. Most of the points raised in the discussion deal with the practical application of the immersion thermocouple to steel-making conditions and the interpretation of the results obtained.

Dr. Reeve mentions the relation of steel temperature in the furnace to skulls in the ladle, particularly in tilting-furnace practice. We have found a correlation between these in our practice, but it is not so sensitive with a slag cover as that indicated in Dr. Reeve's graph (Fig. A) or Mr. Jackson's Table A. In assessing this relationship it is more informative to quote the degree of superheat over the calculated freezing point of the steel than to give actual temperatures. This would explain the sensitivity of the lower-temperature charges to which Dr. Reeve refers. The calculated freezing point of a steel with 0·20% of carbon and 0·60% of manganese is 1520° C., and therefore a temperature of 1590° C. represents only 70° C. of superheat. The ladle cooling would reduce this by 40–50° C., as quoted, thus leaving only a very small margin over the freezing point. The few charges which deviate from Dr. Reeve's curves may have been due to over-oxidation, as this is included in that rather vague term "condition."

I agree with Dr. Reeve that the small variables to which he refers should be considered in applying the temperatures to the teeming of the steel, and I would add a further variable—the ladle temperature. Mr. Land's paper on "The Ladle Cooling of Liquid Steel"<sup>1</sup> deals admirably with these variants.

Mr. Land's remarks regarding the comparative temperatures of the upper surface of the slag and the furnace refractories are very interesting. From data which we have available I have calculated the slag surface temperature on 42 charges for comparison with recorded roof temperatures. The average slag surface temperature was 1637° C. and the average roof temperature 1629° C. There was, however, considerable variation in individual casts, owing to temperature control being exercised. Nevertheless, it would appear, as Mr. Land suggests, that there is a tendency for the furnace to become a tolerably uniform temperature enclosure during the later stages of a heat.

I appreciate Mr. Jackson's contribution, which is of great interest. His Tables and other data from Appleby practice indicate both the usefulness of steel temperature measurement and the necessity for further investigation into some of the points raised. His remarks on steel condition are dealt with in the reply to Dr. Reeve's contribution.

I agree that in quoting figures it is necessary to be assured that these were measured under uniform conditions. The papers

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1941, No. II., pp. 157 P–168 P.  
1944—i PP

already published on this subject pay a tribute to the skill of the melter, in that these conditions are so regularly achieved. Each investigator has stressed the necessity for an active bath in order to attain uniform temperature distribution.

Some preliminary work has been done on the influence of tapping temperature on steel quality. We have compared tapping temperatures with mechanical tests on certain alloy steels from acid open-hearth furnaces. The casts were grouped into temperature ranges of  $10^{\circ}$  C., and each group was correlated with the tests. In this case there was a definite indication that a temperature between  $1610^{\circ}$  and  $1630^{\circ}$  C. gave the largest percentage of good casts. An examination was also made of 600 basic open-hearth charges for which temperature data were available. These were grouped according to qualities and subsequent treatment. The degree of superheat at tapping was plotted against the "sold yield" (*i.e.*, the percentage yield of first-quality material). There was a definite correlation in each case, and it was possible to fix a range of tapping temperatures giving the optimum yield. In neither of these investigations was the nature of the defects examined, and further work is still required in that respect.

As Mr. Jackson states, large deep-bath furnaces do present the problem of the difference in the steel temperature between first and last ladles. With a bath 42 in. deep and a temperature gradient of  $10^{\circ}$  C. per ft. the metal at the bottom would be approximately  $30^{\circ}$  C. cooler than that at the slag/metal interface. It would therefore appear advantageous to ensure that the first ladle was at a temperature sufficiently high to avoid large skulls, which from Table A appears to be  $1590^{\circ}$  C. It is a question of economics to decide whether any increase in refractory costs is compensated for by increased yield of first-quality product.

The question of scatter in the temperature groups below  $1600^{\circ}$  C. with regard to skulling is referred to in reply to Dr. Reeve.

Mr. Jackson also asks if any benefit is derived from tapping above  $1600^{\circ}$  C. in a fixed furnace with a shallow bath and a slag cover. This depends upon the steel quality entirely. The optimum temperature depends upon the steel composition, chiefly the carbon content. Our investigations indicate that, with low-carbon rimming steels, a higher tapping temperature is beneficial, giving a higher yield of first-quality material from the ingot. This does not apply to higher-carbon piping steels, in which a high degree of superheat has the reverse effect.

Much more work is still required before these questions can be fully answered, but indications have been given that the tapping temperature of steel does influence its subsequent properties.

Referring to Mr. Jackson's final question, it is suggested that, in the last analysis, it is the temperature of the steel entering the mould which is the controlling temperature. Any control of this must be exercised in the furnace, due consideration being given

to the subsequent cooling effect of the lander, ladle, tundish or runner.

Mr. LAND wrote in reply: Dr. Schofield's suggestion of an algebraic expression for the sensitivity curve  $S_\lambda$  of the photo-electric cell has interested me very much. When the logarithm of the cell current is plotted against the reciprocal of the absolute temperature, the result is very nearly a straight line. Over the range 1150° to 1750° C. the deviation from linearity is of the order of 5° C. This deviation is due to the fact that the photo-electric cell responds to a fairly broad band of wave-lengths rather than to a single narrow band. The curvature of the calibration curve is clearly determined

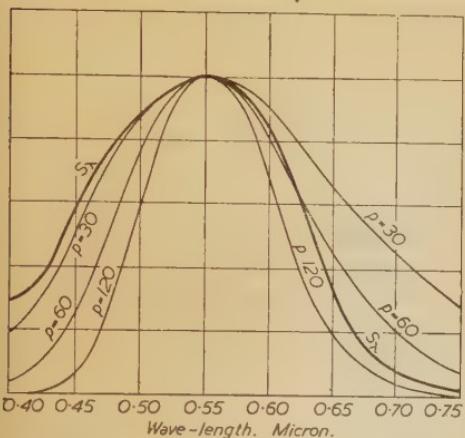


FIG. B.—Photo-Electric Cell Spectral-Sensitivity Curve ( $S_\lambda$ ) compared with a family of Wien-type curves  $\lambda^{-p}e^{-q/\lambda}$  having the same maximum but different values of the parameter  $p$ .

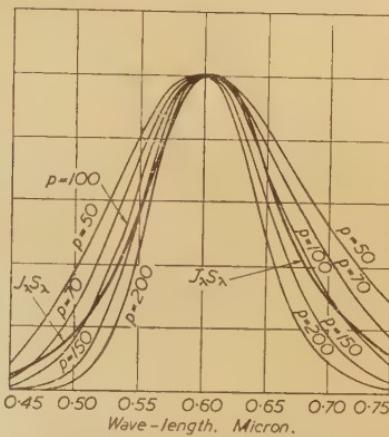


FIG. C.—Spectral Sensitivity multiplied by Radiant Energy at 1800° K. ( $J_\lambda S_\lambda$ ) compared with a family of Wien-type curves  $\lambda^{-p}e^{-q/\lambda}$ , showing satisfactory agreement for values of  $p$  about 100.

by the breadth and shape of the spectral-sensitivity curve of the photo-electric cell. If a parameter could be found which would define the spectral sensitivity it should be possible to deduce the curvature of the calibration curve.

When I attempted to fit a Wien-type curve to the sensitivity curve of a typical cell I was disappointed to find that the agreement was not at all good, as will be seen in Fig. B. However, as Dr. Schofield points out, not all parts of the spectrum are of equal importance, and it appears that the essential test is to fit a Wien-type curve to the function  $J_\lambda S_\lambda$ . This gives a much more satisfactory result, as will be seen in Fig. C. The manufacturer's figures for  $S_\lambda$  are multiplied by the function  $J_\lambda$  (the radiant energy at wave-length  $\lambda$ ) for 1800° K. and plotted as the thick line. The fine lines are a family of Wien-type curves for different values of the

parameter  $p$ . A value of  $p$  of about 100 gives agreement with the  $J_\lambda S_\lambda$  curve which is probably as good as the reproducibility of  $S_\lambda$  from batch to batch of cells.

This is a very promising result, and it seems well worth-while to follow up the mathematical implications of Dr. Schofield's suggestion.

Writing :

$$S_\lambda = \lambda^{-p} e^{-q/\lambda},$$

Dr. Schofield's expression for the effective wave-length  $\lambda_p$  of the photo-electric pyrometer is :

$$\lambda_p = \left( \lambda_m + \frac{C_2}{pT} \right) / \left( 1 + \frac{4}{p} \right),$$

where  $\lambda_m$  is the value of  $\lambda$  for which  $S_\lambda$  is a maximum. Writing  $x = 10^4/T$  and expressing  $\lambda_p$  and  $\lambda_m$  in microns :

$$\lambda_p = \left( \lambda_m + \frac{C_2 x}{p} \right) / \left( 1 + \frac{4}{p} \right) \dots \dots \dots \quad (g)$$

Now it was shown in my paper that if the logarithm of the cell current is  $y$  :

$$\frac{dy}{dx} = - \frac{b C_2}{\lambda_p} \log_{10} e \dots \dots \dots \quad (h)$$

Substituting equation (g) in (h) :

$$\frac{dy}{dx} = - \frac{\left( 1 + \frac{4}{p} \right) b C_2 \log_{10} e}{\left( \lambda_m + \frac{C_2}{p} x \right)}.$$

Integrating, we have :

$$y = \text{constant} - b(p+4) \log_{10} \left( \lambda_m + \frac{C_2 x}{p} \right).$$

Since  $y = \log_{10} i$ , we can write for the cell current :

$$i = \frac{A}{\left( 1 + \frac{B}{T} \right)^n} \dots \dots \dots \quad (j)$$

where  $A$  = a constant depending on the optical system.

$$B = \frac{C_2}{\lambda_m p} \quad (\lambda_m \text{ is now measured in centimetres}).$$

$$n = b(p+4).$$

If we substitute  $\lambda_m = 0.550 \times 10^{-4}$  cm.,  $p = 100$  and  $b = 0.99$ , the agreement with Table VIIIA. of my paper is quite satisfactory, the discrepancy being within the uncertainty of the standards of temperature used in the experiments. The values of the effective wave-length calculated from equation (g) for the temperatures considered in the paper are :

1300° C.	.	.	.	.	.	0.616 . $10^{-4}$ cm.
1500° C.	.	.	.	.	.	0.607 . $10^{-4}$ cm.
1700° C.	.	.	.	.	.	0.599 . $10^{-4}$ cm.

Since  $n$  is of the order of 100 and  $B$  is not exactly known, equation (j) is less convenient than equation (h) for expressing experimental results. Equation (j) is of value if it is desired to extrapolate the calibration curve, and as a means of deriving the calibration directly from the radiation laws and the fundamental properties of the photo-electric cell.

The method which Mr. Barber suggests for calculating the black-body calibration and the effective wave-length of the pyrometer from the tungsten-lamp calibration seems to me to be a distinct improvement on the rather laborious method which I used. Not only is the arithmetic much simpler, but Mr. Barber's method takes account of the variation with wave-length and with temperature of the spectral emissivity of tungsten. His method therefore yields more accurate results and should probably be adopted as the standard method of calculation.

I understand that Mr. Hall, at the National Physical Laboratory, is intending to investigate the cell calibration experimentally to a higher degree of accuracy than I was able to attain. It will be interesting to see just how nearly Mr. Barber's calculations agree with these more precise results when the latter are available.

I was pleased to have Mr. Preston's and Mr. Winch's comments on barrier-layer photo-electric cells, as they have both had intimate experience of these instruments. The warning which they gave regarding the uncertainties of such cells is wise and is no doubt founded on somewhat bitter experience. However, I think that Mr. Preston and Mr. Winch are thinking in terms of the precision which they need in photometric work rather than of the accuracy demanded in an industrial pyrometer. An error of 5° C. (say 4% cell current) is not very serious and even an error of 10% in the cell current would not be disastrous. Furthermore, the use of vacuum photo-electric cells in industrial instruments is not without its own snags and complications. I feel sure that with the cell-selecting device which Mr. Hall has described we shall have sufficient precision for most industrial purposes.

While I will leave most of the comments on fatigue for Mr. Hall's attention, I would mention that I found it impossible to obtain a smooth fatigue curve unless the cell was short-circuited between readings.

With regard to Mr. Preston's question about the hysteresis in the response of the cell to temperature changes, I can confirm his observation. My usual procedure was to fatigue the cell at room temperature until a very steady current was obtained and then to heat the cell quickly to 40° C. It was maintained at this temperature for about 4 hr., readings being taken every few minutes. During the first hour the cell current changed steadily, and then flattened out to a steady value. Sometimes the current would rise about  $\frac{1}{2}\%$  above its final value before settling down. This seems to be the only satisfactory method of working. If the cell is heated

up fairly slowly and then cooled, taking readings periodically, it is inevitable that a hysteresis effect will appear, as the cell never reaches a stable condition. In my early experiments using this technique I obtained curves reminiscent, as Mr. Preston says, of magnetic hysteresis curves.

Mr. OLIVER and Mr. LAND wrote in reply : Many of the questions which Mr. Barratt raised are best answered by reference to current routine practice with the quick-immersion technique for liquid steel temperature measurement in the furnace. The same type of thermocouple (platinum/13% -rhodium-platinum) and the same type of silica sheath were used in our experiments as in routine furnace temperature measurements. So far as we are aware, the only additional hazard in our experiments is that the sheath may be broken by the force of the stream of liquid steel. Provided that the sheath is intact after the experiment, there is every reason to believe, by reference to the extensive experience of furnace temperature measurements, that the thermocouple will be sound. Indeed, the conditions in our experiments were in one important respect more favourable than in the furnace, as the silica sheath was never in contact with slag, which is the chief agent attacking the silica in the furnace. The silica sheaths in our experiments were indeed in much better condition after use than is the case after immersion in the steel in a melting furnace.

The thermocouple wires after use were not subjected to any chemical, spectrographic or other tests for the reasons outlined above, and there was never any sign of discolouration or embrittlement of the wires. Nevertheless, for the sake of maximum precision, new wire was used for every experiment. This precaution would not be necessary when using the method for routine measurements. The useful life of the thermocouple has not been determined, but there should be no danger in using the same wire for five or six measurements.

In reply to the other questions raised by Mr. Barratt, the silica sheath showed a small amount of devitrification after use, and on some occasions the sheath was slightly bent, giving evidence of softening. A single fine twin-bore silica insulator extended almost the full length of the thermocouple,  $\frac{1}{4}$  in. of wire near the hot junction being left bare. The junction was arranged to be in contact with the closed end of the silica tube. No measurements were taken of the temperature gradient along the sheath, and the asbestos tubing provided an adequate safeguard against overheating of the head of the thermocouple.

Mr. Barratt expresses surprise that the rare-metal thermocouple could be used in contact with fused silica at high temperatures without contamination. There is no danger of contamination by silica unless certain reducing gases which reduce the silica to silicon are present. Under the conditions of our experiments no

such gases were present, and there was therefore no danger of contamination from this source.

Mr. HALL wrote : In reply to Mr. Preston, I have not at present made any experiments to show whether the drifts caused by exposure to red and green light are independent. In the measurement of brightness temperatures (our sole concern at the moment) the point is of no practical importance, but it will clearly need study if barrier-layer cells are to be used for colour-temperature measurement.

I have no results to show whether a curve similar to that in Fig. 10 could be produced by open-circuiting the cell instead of cutting off the light, but it will be noted that the initial output of a "dark-adapted" cell was unchanged after it had been exposed to the standard illumination for 2 hr. on open circuit.

With reference to Mr. Land's remarks concerning the non-linearity of the calibration curve produced by the change in effective wave-length with temperature, I should be a little diffident about fitting parabolæ to the observations plotted in Fig. 3. Perhaps a surer foundation will be forthcoming as a result of calibration observations which we propose to undertake in the near future, using cells selected for minimum drift.

Mr. Land's method of plotting drift, using a logarithmic scale of time, is open to the objection that extrapolation suggests that the cell never reaches a steady state. An alternative would be to use a logarithmic scale for  $\Delta(\log_{10} \mu A)$ , measuring the differences ( $\Delta$ ) from the final steady value. Clearly, this method can only be used when the observations have been extended over a considerable period so that the final value can be estimated fairly closely.

Taking the curves of Fig. 4, the observations for cell 9 fit a straight line quite well when plotted in this way. The curves for cells 6 and 7, on the other hand, are much steeper in the initial period, showing that the rate of drift during the first 10 min. of exposure is much greater than would be expected from a simple logarithmic law deduced from the remainder of the curve. The whole curve could, no doubt, be closely fitted by a combination of two logarithmic equations having widely different exponents, and, if, as Mr. Preston suggests, the drift mechanism can be separated into two parts, it seems not unreasonable to suppose that the two components should drift at different rates.

Mr. Land's suggestion that the drift should be specified in terms of that occurring between the ends of the first and hundredth minutes of exposure does not necessarily give an indication of the behaviour of the cell during the first few seconds, but is probably sufficient for a simple acceptance test.



Further discussion on the  
**FOURTH REPORT OF THE OXYGEN  
 SUB-COMMITTEE**  
 OF THE  
**COMMITTEE ON THE HETEROGENEITY OF  
 STEEL INGOTS.**

*Paper No. 22/1943 of the Committee on the Heterogeneity of Steel Ingots (submitted by the Oxygen Sub-Committee).*

This Report was included in the programme of papers for the Autumn Meeting of the Institute held on October 14th, 1943, and will be found, together with the correspondence to which it gave rise in the *Journal of The Iron and Steel Institute*, 1943, No. II., p. 231 p. Later it was discussed at a Joint Meeting of The Iron and Steel Institute with the Sheffield Society of Engineers and Metallurgists and the Sheffield Metallurgical Association held at the Royal Victoria Station Hotel, Sheffield, on Saturday, December 4th, 1943, at 2.30 P.M., under the Chairmanship of Professor J. H. Andrew (Member of Council of The Iron and Steel Institute and Past-President of the Sheffield Society of Engineers and Metallurgists). The Report was presented by Dr. T. Swinden, Chairman of the Oxygen Sub-Committee; a summary of its contents, the discussion and replies are recorded below.

#### SUMMARY.

Since the publication of the Third Report of the Oxygen Sub-Committee (see *Journal of The Iron and Steel Institute*, 1941, No. I., p. 295 p) the further continuance of the war has interfered with the smooth and regular prosecution of the various researches in hand; several additional problems have, however, been investigated. Considerable attention has been devoted to the determination of gaseous elements other than oxygen, *i.e.*, hydrogen and nitrogen, as they occur in solid materials. The fundamental aspects of the residue methods and their application to a series of alloy steels have received further examination, and the determination of the gas content of liquid steel, in contradistinction to solid finished products, has been investigated and will continue to be a problem of high priority. The vacuum fusion method continues to be applied to specialised problems such as the surface film on metals. The present Report is in five Sections. The first is introductory.

Section II. is divided into three parts which deal with the determination of oxygen, hydrogen and nitrogen, respectively. There are nine papers in Part A of this Section. In the first, H. A. Sloman examines the applicability of the vacuum fusion method to the determination of oxygen, hydrogen and nitrogen in a series of alloy steels and ferro-alloys used in steelmaking. In the second, T. Swinden, W. W. Stevenson and G. E. Speight report the results of applying the fractional vacuum fusion method to the determination of oxygen in weld-metal deposits; from these results it is readily seen that the method furnishes far more information regarding the features of each particular deposit than does the direct total method. In the third, N. Gray and M. C. Sanders describe a modification in the procedure for the aluminium reduction method of determining oxygen in tungsten-bearing steel and in 4% silicon transformer iron. In the fourth, E. W. Colbeck and S. W. Craven describe experiments

on the effect of increasing the temperature in the chlorination method on the recovery of oxide inclusions from fully killed steels. In the fifth, T. E. Rooney presents a critical summary of the work carried out on the alcoholic iodine method. The next three papers all relate to that method also. In the sixth, T. E. Rooney deals with the determination of the water content of methanol and its effect on oxygen determinations by the alcoholic iodine method. In the seventh, G. E. Speight discusses experiments on the composition of extracted non-metallic residues from high-carbon and -phosphorus steels. In the eighth, T. E. Rooney describes the examination and analysis of residues from the alcoholic iodine method. The last contribution to Part A is a note by W. Westwood on oxygen determinations in pig and cast iron by the aqueous iodine method. Part B contains four papers. In the first of these W. C. Newell briefly reviews the development of the present-day methods of determining hydrogen in steel. The other three papers contain detailed descriptions of the apparatus in use at three different laboratories for determining hydrogen by the vacuum-heating method. Thus, W. C. Newell describes that at the Brown-Firth Research Laboratories; W. W. Stevenson and G. E. Speight that at the Central Research Department of The United Steel Companies, Ltd., Stocksbridge; and E. W. Colbeck and S. W. Craven that at I.C.I. (Alkali), Ltd., Northwich. Part C contains three papers all by T. Swinden. In the first, a general account is given of the principal methods used for the determination of nitrogen in steel. In the second, the general applicability and possible sources of inaccuracy of the vacuum fusion method are discussed. The third contains a brief outline of the development and modifications in procedure recommended for the determination of nitrogen in iron and steel by distillation methods.

Section III. deals with the application of the methods described in the preceding Section to several specialised problems. H. A. Sloman and A. J. Cook describe the experimental technique developed at the National Physical Laboratory for the production of low-oxygen-content iron bar. H. A. Sloman and T. E. Rooney next report on a systematic study of the surface oxygen on different types of specimens of iron and steel by the vacuum fusion and alcoholic iodine methods. T. E. Rooney and F. W. Jones give details of an examination of a number of acid Bessemer, basic Bessemer and basic open-hearth rimming steels by the alcoholic iodine method and of the identification of constituents of the residue by X-ray methods. In an Appendix to the last paper, T. E. Rooney and H. A. Sloman describe the determination of total oxygen by vacuum fusion on a residue prepared by the alcoholic iodine method. W. H. Hatfield and W. C. Newell publish and comment on the results obtained for the gas content of the raw materials used in steelmaking. W. W. Stevenson and G. E. Speight describe experiments with five well-known methods for the determination of oxygen in iron and steel and study their applicability to the determination of oxygen in slag particles in ferrous materials. This is followed by two papers on transformer iron in which N. Gray and M. C. Sanders study the behaviour of 4% silicon transformer iron in the aluminium reduction method in a hydrogen atmosphere, and C. S. Graham and C. W. Short examine the behaviour of this iron in the aluminium reduction method under reduced pressure. Next, J. G. Pearce records the total oxygen contents of twenty-nine pig irons determined by the aluminium reduction method and of seven of the same group by the vacuum fusion method. In the last paper of this Section T. Swinden presents and comments on the results obtained by the accepted procedures for the oxygen, hydro-

gen, nitrogen and non-metallic-inclusion contents of a series of alloy steels.

In Section IV. descriptions are given of the methods developed for the sampling of liquid steel and the determination of its gas content, T. Swinden and W. W. Stevenson dealing with the determination of oxygen by a "bomb" method, while W. H. Hatfield and W. C. Newell describe the notched chill-mould method and the balloon-tube method for determining hydrogen.

Section V. consists of a general summary of the Report.

### DISCUSSION.

Dr. T. SWINDEN (Member of Council; Chairman of the Oxygen Sub-Committee; The United Steel Companies, Ltd., Stocksbridge, near Sheffield) : I submit this Report with very great pleasure. This is a piece of collaborative work, and I would emphasise the value of work of this kind. It is very important that we should have this in mind at the present time, in view of certain reorganisations that are likely to take place in the control of our national scheme of research.

It is my first and pleasurable duty, as Chairman of the Sub-Committee, to thank the Members of the Sub-Committee for the way in which they have worked. Great credit, I think, is due to men who are devoting what might otherwise be a certain amount of leisure to work of this kind for the benefit of their fellow-men in the industry. Our thanks are also due to the companies who have allowed their resources to be devoted to this work.

Dr. Swinden then gave a brief summary of the scope and contents of the Report, and added : I would reiterate that we feel that methods have been laid down for the accurate determination of the oxide constituents and hydrogen and nitrogen. Some of the earlier chemical methods which we hoped would be applicable to routine control have, in my opinion, merged into what I would call research methods. To separate these inclusions and determine their form of existence in the steel and so forth with real accuracy is a very intricate chemical operation. On the other hand, while the vacuum fusion method or the aluminium reduction method will give accurate figures for total oxygen, and the former also figures for hydrogen (which, in my opinion, mean very little indeed), and figures for nitrogen (which are reliable and accurate), they do not carry us very much further along the road towards producing better steel or tell us much more about the inclusions than is obtainable by thorough metallographic examination. They are a useful check on the metallographic observations, but beyond that, while this was work which had to be done, I do not think that it carries us very much further towards making better steel or explaining the discrepancies between this and that steel.

I feel strongly, however, that we have laid the foundation for further work, some of which is now in progress, for the control of oxygen during steel manufacture. It seems to me common sense

that, as oxygen is the most important reagent in all steelmaking processes, sooner or later we must have a method for determining oxygen during the process of steelmaking. When that has been established, the results will mean something in the actual control of the steelmaking process.

Mr. E. W. COLBECK (I.C.I. (Alkali), Ltd., Northwich) : I think that Dr. Swinden, in his excellent survey of the recent work of the Sub-Committee, has rather underestimated the usefulness in industry of some of the methods which have been worked out. Under war-time conditions it is, of course, difficult to give chapter and verse for such a statement, since in so many cases the applications are connected with work for Service departments which cannot at the present moment be disclosed. I can, however, assure you that the methods developed by the Sub-Committee for the determination of oxygen, nitrogen and hydrogen have proved of considerable value during the present war. There has been a wide variety of problems which the work of the Sub-Committee has helped to solve—problems connected with welding, with high-pressure reactions, with the manufacture of pure metals, &c.

I should like to pay a special tribute to the work carried out in the different laboratories which have developed methods for determining oxygen, nitrogen and hydrogen by the vacuum fusion method. All the Members of the Sub-Committee feel that this method can justifiably be considered as a referee method for these gases and has therefore provided us with an invaluable yard-stick by which we can measure our own results when we have been operating some other method.

In particular I should like to refer to the value of the work which Dr. Newell has carried out on the determination of hydrogen by the vacuum-heating method. This method has proved particularly useful and there have been a number of industrial problems, outside the normal ones of the steel trade, which it has solved. There have been cases in which it has been necessary to determine accurately hydrogen in the surface layers of high-pressure vessels, and by using this method it has been possible to study the attack of hydrogen on alloy-steel forgings.

The Section of the Report which deals with nitrogen provides us with an excellent summary of the present state of knowledge with regard to the determination of this element. Modern research is drawing our attention more and more to the possibilities of nitrogen as an alloying element. I feel that we would be well advised to speak of alloy systems containing nitrogen not as iron-nitrogen, chromium-nitrogen, &c., but rather as iron/iron-nitride, chromium/chromium-nitride, &c. The effect of nitrogen, particularly in the higher alloy steels, has great possibilities, but it is only fair to say that our imperfect knowledge of its effects may result in the production of seriously unsound steel. The work

which Dr. Swinden has summarised in connection with methods of analysis for this element has been of particular value in the case of complex alloy steels.

Finally, although I have no direct experience myself, I believe that the work which has been carried out on the determination of oxygen during the actual steel melting process is of fundamental importance. There is no doubt that when further experience of the different proposed methods—the balloon method, &c.—has been obtained, information will be steadily acquired which will prove to be of fundamental and first-rate importance in controlling what, after all, is the most important consideration, namely, the manufacture of high-quality steel.

Dr. SWINDEN : It is most refreshing and encouraging to hear Mr. Colbeck illustrate the usefulness of this work, perhaps in directions which are not so immediately apparent to those of us who are engaged mainly in steelworks. I hope that I did not sound unduly pessimistic about the value of the work. I am under no misapprehension so far as that is concerned, and if it had been only to determine the applications and limitations of the various processes, that work would have been well worth-while. All these methods have constructive value. What I did endeavour to point out, however, was the necessity, particularly from the steelmaker's point of view, of being able to determine these gases during manufacture, and not only by *post-mortem* examinations.

I can assure Mr. Colbeck that the determination of hydrogen is very much in our minds. Anyone who has read the papers coming from the committee which is dealing with hair-line cracks and who has studied the recent reports on cracked welds will readily appreciate that. The same is true of nitrogen; and, having regard to Mr. Colbeck's own contributions to that subject, we do in several directions regard nitrogen as an alloying element, and we know of its application in certain classes of steel of ordinary mild-steel type for promoting good finish in machining and so forth.

I entirely endorse Mr. Colbeck's appreciation of the work which has been done, particularly in the determination of hydrogen and nitrogen as well as oxygen. We may not have brought out sufficiently in the Report the great importance of determining hydrogen at the time of casting. Dr. Newell has dealt with that to some extent, but I did casually say that I did not think much of the hydrogen figures that were reported. The reason is that, when you look at these figures and consider all sorts of steels made by all sorts of processes, you find that the variation in the hydrogen content of the cold sample is very small. If we believe that hydrogen is an important factor in these various directions which have been indicated, then it does mean, I think, that the hydrogen content of the steel at the time of casting is the more important factor, and that in due course we ought to be able to correlate those data with

some of the well-established differences in the behaviour of steel made by different processes.

Dr. W. C. NEWELL (The Brown-Firth Research Laboratories, Sheffield) : Here are two exhibits which I have brought along to show more clearly the methods which we have employed for sampling liquid steel. We knew early on that the hydrogen content of a solid steel sample depended somewhat upon its previous history, and we therefore set out to determine the hydrogen content of liquid steel, as a guide to the steel melter as well as to indicate the possible effects of hydrogen during the solidification and cooling of the steel.

To retain as much of the hydrogen in the sample as possible the obvious thing to do was to quench the molten steel sample rapidly, and for this purpose we initially used a sample poured into a "carbometer" mould. Such samples, however, when cold were usually in such a hardened state that they could not be machined with sufficient ease and rapidity. This difficulty was overcome by casting this notched test-piece (*see Fig. 26, Plate XXII.*<sup>1</sup>), samples from which could be snapped off easily.

So far so good, but we still did not know whether or not even under those conditions some hydrogen had been lost from the liquid steel during sampling, and if only to settle this point some test was necessary to collect and examine any gas given off during the solidification of such a small sample. Needless to say, we hoped that no gas would be evolved under those conditions so that our simple sampling method would be adequate, but we were disappointed. We found that if the hydrogen content of the liquid steel was above certain specified limits, then some hydrogen was evolved during solidification and cooling. This balloon-tube device (*see Fig. 27, loc. cit., p. 410 P*) was designed to quench a small sample rapidly under a uniform pressure of one atmosphere. The results obtained by it are very encouraging, and I hope that as a consequence of this publication others may be stimulated to use and improve the device. (Dr. Newell then explained the details of its operation.)

Mr. A. ALLISON (Messrs. J. J. Habershon & Sons, Ltd., Rotherham) : I should like to ask whether the Sub-Committee have formed any view as to whether oxygen is symptomatic or causative. Are the Members of the Sub-Committee of opinion that the presence of so much oxygen in steel is an indication of its mode of origin and treatment, or does the presence of the oxygen have a bearing on the physical properties of the material? For example, in making a cast of properly killed acid open-hearth steel our endeavours have always been to remove all the oxygen, but then, having got the bath free from oxygen, the metal is tapped into a ladle, whereby

<sup>1</sup> *Journal of The Iron and Steel Institute*, 1943, No. II.

oxygen is churned into the metal. In the case of a fairly large ladle of steel, it usually requires 30 min. or even longer to cast into ingots, and we may assume that by that time the metal has rid itself of oxygen. Unfortunately, in casting that steel (which we might assume to have rid itself of oxygen) into ingots, we are going again to churn more oxygen into the material. It seems to me that there is a close analogy there between the oxygen contents and the leaded ingots which have been described by Dr. Swinden and others in recent papers, the only difference being, I take it, that lead is insoluble and happens to be a liquid of about the same specific gravity as steel and thereby remains mixed, whereas oxygen is soluble.

I should not like to suggest the experiment of allowing a ladleful of steel to solidify in the ladle to ascertain whether it was entirely free from oxygen or not. On the other hand, taking the crucible steel process, the pot is porous and there is carbon monoxide there, but we might reasonably assume that the steel in the crucible is free from oxides and oxygen. Unfortunately, again, although the crucible-steel ingot is probably the finest ingot that is ever made, during casting oxygen is churned into it. I do not know whether, by introducing gas into the mould, attempts have been made to cast ingots in an entirely neutral atmosphere to ensure that the liquid steel from the nozzle was not in contact with oxygen until it was in the mould; it would not be an elaborate or expensive experiment to allow a pot of crucible steel to solidify and then determine the oxygen content, if any. I am not overlooking the experiments reported by Dr. Swinden on bubbling nitrogen through small ingots, but I am dealing with ingots on an industrial scale.

As we all know, each type of steel—acid open-hearth, basic open-hearth, acid Bessemer and so on—has its own special characteristics. Have the Sub-Committee any reason to think that oxygen might be connected with any of these varieties? For example, it is understood that acid Bessemer steel of dead soft quality has markedly good free-cutting properties, and it is also well known that basic open-hearth steel of low carbon content has distinctly bad free-cutting properties. Have the Sub-Committee any views on that?

On p. 396 P the Report makes what I consider to be a very wise suggestion, namely, that "it is not unlikely that there is an optimum oxygen content for steels of different classes." I think that that will find general acceptance, in view of what we know about the controlled oxygen contents of rimming steels, for example, and we have the shallow-hardening steel and others which deliberately are not completely killed. Have the Sub-Committee any views on that?

All research is subject to the risk of exploring a field which ultimately proves to be barren, but at all events the ground has been mapped out, so that those who come after us will have no occasion to explore those fields again. I would not suggest that

that is the case here, in view of what I have said about the possible optimum oxygen content, but we have to keep that possibility in mind.

There is a further point which I should like to raise. In selecting steels to comply with specifications we have had the experience of taking a cast which undoubtedly complied with the specification, but of which possibly the ultimate stress was on the extreme low side of the specification and the elongation rather high; another cast, of apparently similar analysis, would give an ultimate stress on the high side of the specification, with a lower elongation, although both steels ought to have come right in the middle of the specification. Have the Sub-Committee any views on that point?

If I may take advantage of the invitation given for suggestions for further work, I have felt for some years that, while pure research is obviously of intense value, frequently scientific men can gain information by making use of the results obtained in experience. In no one specific instance could it be said that the information gained was scientific, because one did not know all the fundamental data concerning the material in question; on the other hand, when information on an abstruse point was wanted and experience from many cases all pointed in the same direction, one was justified in drawing a conclusion from that. I suggest that the Sub-Committee might usefully, from the oxygen standpoint, and perhaps from the nitrogen and hydrogen standpoints also, examine cases (which we all know of) in which the results of the mechanical tests of a material are unusual for the known analysis. They have in the Report dealt with a silicon transformer iron, and I think I can see that they are looking for something of the kind there. The Sub-Committee could possibly examine casts the tests of which are unusually good or unusually poor and study them from the oxygen standpoint, with a view to ascertaining the final information for which we all seek.

Dr. SWINDEN : We hope that replies to questions will be given by the authors of the Sections of the Report mainly concerned. It seems to me that the Section in question here is the one for which I am personally responsible, namely, the short introduction to Section IV.; but the Sub-Committee reserve the right to add to these replies in due course.

As to whether the oxygen content is symptomatic or causative, I would emphasise that the chemical methods only separate *inclusions*. Our original idea was, of course, that by these methods we could get the oxygen in the inclusions; by vacuum fusion we get the total oxygen (namely, inclusions plus oxygen or oxide which might be in solution), and by difference we would get a figure which might be related to steelmaking processes or to the correlation with mechanical tests to which Mr. Allison has referred.

Those who have read the previous three Reports know that our

big trouble has been that the vacuum fusion method usually gave lower results than the chemical methods for inclusions, and we considered that we had accomplished something when we got reasonable agreement between the two. I ventured to say in the last Report that that did not necessarily mean that we had got the right results, because I have always had a feeling, rightly or wrongly, that there is still something to be found out about the possibility of an optimum oxide content. In saying that I have in mind the fairly well-known characteristics of what, for the want of a better term, we have called "over-reduced steel," that is to say, steel which has been deoxidised to the fullest extent, as, for example, in the acid open-hearth process, where you have worked up to a dead killed bath; you have run up a high temperature, you are throwing silicon back from the slag, and then you add further deoxidisers—aluminium, titanium or zirconium—and you get the steel into such a condition that, no matter how hot it is, it will not run freely. It will not, for example, run uphill or into small steel castings, and it is a well-known fact that to make that steel run more freely you add some oxide. Whether that is entirely a matter of surface tension or surface films still requires to be proved, but the practical observations, I think, are quite well established, so that I appreciate Mr. Allison's support of the possibility of there being an optimum oxide content.

With regard to casting in a neutral atmosphere, I do not recall work in that direction, but a great deal has been done on casting *in vacuo*, and there is, in particular, some interesting American work, showing differences in grain size between similar steel cast *in vacuo* and cast normally, which in turn was applied to the nucleation theory of alumina in connection with grain-size control.

I appreciate Mr. Allison's suggestion regarding future work, and, at least so far as my own company is concerned—and I imagine that this would apply to all the other collaborating firms—it is at present, of course, our whole business to be applying these methods in a routine manner not only to finished samples but also to samples taken during manufacture, to see how we can correlate those data with different characteristics of the cast, with defects or with anomalies in physical properties. Mr. Allison mentioned acid Bessemer steel as being free-cutting. Rightly or wrongly, we have attributed that to nitrogen, and it is well known that at least one large American company is adding nitrogen by means of ammonium nitrate or cyanamide and obtaining a nitrogen content in basic open-hearth steel similar to that of Bessemer steel. It uses that steel in its own plant for certain components as a freer-machining steel. The trouble is that we are determining oxygen mainly in the non-metallic inclusions, silicates and so on, and that complicates a true comparison of oxide contents of Bessemer and open-hearth steel. So far as inclusions are concerned, a really accurate study of their identification, composition and distribution can be

carried out very largely by metallographic work; frankly, I regard oxygen determinations in the meantime more as confirmatory in that direction than as dealing with the finer point of determining the precise rôle which oxygen plays in controlling the physical characteristics of the material, as distinct from the influence of inclusions.

Dr. R. J. SARJANT (Messrs. Hadfields, Ltd., Sheffield): I should like to speak more or less from the point of view of the looker-on. The work which has been done is certainly work of which the Sub-Committee should be proud, and represents, I think, the first stage of a survey of a very difficult field of investigation. Anyone who has had anything to do with vacuum methods knows how difficult it is even to make the apparatus work. It is a special technique, and therefore the methods require time before they begin to yield results. Further, so many factors are involved that a large number of observations have to be made before you begin to see daylight. I think that the Sub-Committee have traversed a very important first stage in building up a technique of determining the oxygen and the other gases.

The first stage has only been the determination of the total quantities. In the case of oxygen, of course, the Sub-Committee have attempted to determine how much oxygen is combined with individual elements, and they have obtained certain results from that, but when one comes to consider what is the bearing of those contents on the properties of the steel I feel that that is a more difficult problem, because the results probably depend on where the oxygen is in the steel. This is the case, in my opinion, in regard to hydrogen. The quantity of hydrogen that can be responsible for rather important changes in the steel is very small, and the problem of distribution is the major one.

I was very interested to see the little instrument which Dr. Newell showed us. It seems to me to be a very promising line of attack on the subject, though I feel that, in taking a sample of gas, once you have taken the steel out of the furnace you lose an observation which may be of very great value. How much gas is coming out of the steel while the sample is being taken and while it is freezing down to the temperature at which the sample is taken? It would be very much better if that sample could be taken in the furnace, and I think that Dr. Newell has given us a lead as to how that could be tackled. I imagine that it would not be a very difficult technique to insulate the apparatus and put the whole of the container actually into the furnace, in a manner similar to that employed with the couples used for immersion pyrometry, where the technique is quite successful. Would there be any practical difficulties of sampling under such conditions? Dr. Newell is to be congratulated on producing such a simple and, as it seems, very useful piece of apparatus.

I should like to know whether the Sub-Committee have yet considered the question of studying the gas content of slags. That may be a useful line of investigation. Basic slags are sometimes exceedingly gassy. In the ordinary smelter's method of examining the quality of acid steel by small spoon samples, an empirical technique has been worked out in regard to the cutting of the test-piece on the edges. Those marks on the test-pieces are undoubtedly due to gas, and they are exceedingly susceptible to temperature.

When the Sub-Committee have had an opportunity to multiply their observations and to tie them down to some of the additional technical data on the quality of steel on the lines suggested by Mr. Allison, fruitful results could be expected. I should like to see, for example, what is the relationship between temperature and gas content under differing operative conditions. We know that very hot steels are sometimes very gassy, and yet it has been said that very hot steels are better than cooler steels and can be made without excessive gas content. I think that ultimately the whole of the steel industry will have cause to congratulate itself on having started this new piece of work.

Dr. SWINDE : I thank Dr. Sarjant for his most interesting contribution. There have been several methods for attempting to determine the total gas in liquid steel, and notably that of Herasymenko and Dombrowsky,<sup>1</sup> but with equipment which did not strike me as readily usable on the stage, though as a laboratory piece of equipment it was quite good. During a trip to America I saw equipment at the Canton Works of the Republic Company, where a somewhat similar system had been applied, but with a long tube, about 6 ft. in length, which they evacuated, and which was fitted with a sealing plug in the bottom ; when the latter melted, the steel shot up the tube, and they were applying the same general technique as Dr. Newell does in his apparatus.

To deal with the gas content of slags is again to broaden the terms of reference of the Sub-Committee. The Sub-Committee were originally appointed to determine methods for estimating these gases in steel. They extended their scope, I think quite properly, to at least a demonstration of the usefulness of the methods, but they hope that the Ingots Committee, of which they are a Sub-Committee, and indeed the whole industry, will now of their own volition endeavour to apply and use these methods and find out more about steelmaking processes and the properties of steel. We have not as a Sub-Committee dealt at all with the gas content of slags, but that is a very useful suggestion ; work on slag samples comparable with steel samples and taken at the same time would, I think, be very useful. In certain other directions the gas content of slags is exercising our minds very much indeed, particularly with

<sup>1</sup> *Archiv für das Eisenhüttenwesen*, 1940, vol. 14, p. 109.

regard to foaming slags in basic open-hearth furnaces and in certain other directions.

The last point raised is both interesting and complex. I do not think that there is much doubt that the solubility does increase with temperature, but an adequate temperature is a *sine qua non* in making clean steel, and I would repeat that what we are determining are the inclusions in steel; therefore, although the gas content taken at the time of pouring might be higher, the oxygen content, for example, as determined on a cold sample might well be lower, because there would be less inclusions.

Dr. NEWELL: I thank Dr. Sarjant for his encouraging remarks. Further to his query I would reply that we have had it very much in mind to sample liquid steel direct from the furnace or ladle. Already, working with the balloon-tube method, we have taken samples from the ladle, and we intend to go on to sample direct from the furnace. The manner of operation has been to clamp a balloon-tube, well wrapped in asbestos-wool, to a 20-ft. length of bar, which is held in the hands like a fishing rod. Some strength and careful handling are necessary in order to insert the tube into the metal in the proper manner, but the real difficulty is to obtain a patch of bare metal surface free from slag. We have not, as yet, deliberately examined slag for its gas content, but we could have done so, as some of our intended metal samples turned out to be slag. It would seem, therefore, that if the gas content of slag is of real interest, then we could apply this method to slag examination. The depth of immersion of the tube is not of great importance, as the steel rod within the tube prevents molten steel from rising above the level of the lower end of this rod.

Mr. A. A. MUNRO (Imperial Chemical Industries, Ltd., Sheffield): The amount of gases persisting in solid steel may, by analysis, be small, nevertheless each may have a very serious effect, not only in the early stages of manipulating the steel but also in the life of the finished article.

The Oxygen Sub-Committee, dealing with one side of the picture, have already done useful work, but by further enlarging their field to include all the gases in steel much more valuable data should become available.

The basis from which to build up any theory can be agreed by taking analyses at different stages of manufacture, but I would suggest the best place is in the melting furnace. Provided that this could be standardised at each works, sufficient information could be found to guide those responsible for the steel in the first case.

There is no doubt that users of steel are being forced by metallurgists to become greatly interested in the subject of gases in steel, and the day may not be far off when specifications may call for such analyses. As gases, like other inclusions in steel, cannot

altogether be avoided—neither may it be advantageous to reduce them to a negligible figure—I feel it is the duty of the manufacturer to give some guide as to the amount permissible plus the balance required to avoid further troubles in fabrication or service.

Only by extensive and thorough investigation on agreed methods can this be made possible, but it should be possible with all the opportunities seemingly available to those carrying out the researches.

Dr. SWINDEN : I would impress on Mr. Munro that the respective gases must be determined separately and their effect must be studied separately. There does not appear to be any virtue in regarding the gases in total when studying their effect.

It has already been stressed that the future programme of work will be concentrated on determining gases during the various stages of steel manufacture. On the other hand, it is premature to talk about standardisation of control by gas determinations at the present time.

Similarly, it is premature to specify gas contents, but the day may come when, in the light of fuller information and of wider application of the technique of determining gases, this will be yet another feature of steel specifications.

In the meantime it is emphasised that the subjects of gas determination and the influence of gases are still in the research stage.

Dr. W. R. MADDOCKS (The University, Sheffield) : I am particularly interested in that part of this Report for which Mr. Speight is responsible, and which concerns alcoholic iodine experiments on high-carbon steels (p. 257 p.). At the University a fair amount of work was done on this part of the programme, work which unfortunately had to be stopped, and it was noticed then that the iron fraction from the alcoholic iodine separation of high-carbon steels was impossibly high and had no relation at all to any theoretical basis of the oxygen content in high-carbon steels. Double extraction (that is, putting the precipitate through a fresh iodine solution) made the iron fraction slightly lower, but did not take it out of the realm of absurdity, and it was felt that probably the heat treatment of the steel sample itself was important, in so far as the dissolution of the iron carbide in the sample might be incomplete. Therefore, some pieces were normalised, sub-critically annealed and quenched; all the quenched steels had a very much higher iron fraction than was given by any of the other heat treatments. It is possible in such a case that, as Mr. Speight mentions, the incomplete dissolution of the iron carbide is the cause of the high results, but after quenching a piece one would not expect the iron carbide to be so massive that it would not dissolve; after quenching, one would expect it to be in the very finest state, so that it is doubtful whether incomplete dissolution is the answer.

The  $P_2O_5$  fraction of the quenched steels was abnormally high, whereas that of the normalised and of the sub-critically annealed steels was normal. It is possible that the iron phosphide, or rather the phosphorus, was in a different state after quenching and after sub-critical annealing. I think that Mr. Speight is right in suggesting that it is a question of adsorption, since the carbon in the residue after extracting the quenched specimen with iodine was extremely voluminous and in a very fine state of division. Such conditions are ideal for adsorption to take place. I think that Mr. Speight is to be congratulated on looking into the problem so well. The question of the  $P_2O_5$  residue has still to be solved, but, no doubt, it will be solved in time.

One has the feeling, having read the Report, that the methods of analysis are well established, and one wants to look further ahead and see what value the methods of analysis are going to be to the metallurgist, and mainly to the ferrous metallurgist. One immediately thinks of steelmaking, since it is a process in which oxidation plays an important part, and also one in which oxygen, as such, is a deleterious constituent of the steel. The other part of the steelmaking process which immediately springs to mind is the deoxidation stage, for deoxidation without a complete knowledge of the form in which the oxygen is present in steel is an impossibility. For example, one cannot deoxidise a steel any further, though the oxygen content may be high, if the oxygen is present as alumina; it must be known, therefore, whether it is present as alumina or as ferrous oxide.

If, with those ideas in mind, the various methods of analysis are considered, the vacuum fusion process undoubtedly gives a completely accurate result for the total oxygen value, but it does not convey much more; it does not give that little bit of extra information which is urgently needed in steelmaking processes, particularly from the deoxidation point of view. It may indicate that the oxygen is high, say in an unskilled steel, but it merely indicates, as Dr. Swinden has stated, whether the steel is "clean" or "dirty." The alcoholic iodine method gives much more detailed information about the mode of existence of the oxygen, but the method is strictly limited to certain types of steel and by the time it takes to determine the oxygen value.

To my mind, a method which will combine the accuracy of the vacuum fusion method with the detailed analysis of the types of oxide present which the alcoholic iodine process gives is the ideal. The fractional vacuum fusion process seems the obvious choice, having regard to the detailed information required plus the accuracy which is essential, and I venture to say that this process will in the future play an increasingly important part in the determination of oxygen in steels. It is the only process which will give, in anything like a reasonable time, the state of occurrence of the oxygen in steel in the open-hearth furnace. All other methods, such as

the aluminium reduction methods, though giving accurate total oxygen values, cannot determine the form in which the oxygen exists.

In the case of hydrogen determinations, the degree of accuracy obtainable is of a very high order, both by the vacuum-heating method and by the vacuum fusion method, but one feels that, in view of the work already done by Mr. Sloman and by Dr. Newell and that going on at Sheffield University, the use of small samples is bound to lead to results capable of very serious misinterpretation. I am glad to see that Dr. Newell has started taking samples in the furnace, and has not really bothered about the small sample which has been lying about his works or laboratory for a period of months or years. I think that the amount of hydrogen in a small sample is determined rather by the size of the sample than by the amount of hydrogen which was originally present.

Mr. G. MURFITT (Messrs. Wm. Jessop & Sons, Ltd., Sheffield) : I have been very interested in the determination of nitrogen, and am very much indebted to Dr. Swinden for his neat summary of the methods. On p. 320 P Dr. Swinden says we must not overlook the possibility of the development of a technique whereby the distillation can be entirely omitted. I think that that would be a great step forward ; after complete solution of the sample has been achieved, the distillation causes most trouble. I believe that the Germans have done some work in this direction already, and I shall be very interested to follow this development.

I was very interested to read Section III. of the Report, perhaps most of all Section III. (e), and I particularly admire the persistence with which the workers at Stocksbridge followed up the difficulties of the reduction of the samples of acid and basic slag (pp. 372 P-373 P).

In the description of the gravimetric determination of alumina (p. 403 P) no mention is made of the use of sulphuric acid, yet we have it on the authority of Gregory and Stevenson<sup>1</sup> that the fluoride of aluminium is volatile.

Dr. SWINDEN : It is agreed that the fluoride of aluminium is volatile, and that when dealing with residues containing alumina which has been formed by ignition of other aluminium compounds at, say, 900–1000° C., there is a definite possibility of the formation of aluminium fluoride in the absence of sulphuric acid. However, in this method the alumina has been produced at steelmaking temperatures, say, 1600° C., and is much more resistant to decomposition by hydrofluoric acid. Consequently, in view of the necessity for speed in this determination, the sulphuric acid addition is omitted.

<sup>1</sup> "Analysis of Metals and Alloys," 2nd edition, p. 221. London and Glasgow : Blackie and Son, Ltd.

Dr. SARJANT : I should like to throw out a very controversial suggestion regarding a matter referred to by Dr. Swinden in his reply to Mr. Allison, namely, his very interesting comment about the effect of vacuum-casting on the grain size. I have not been able to understand why, if you vacuum-melt your steel and cool it *in vacuo*, the grain size should be entirely governed by the amount of nuclei there. I would suggest that it might even be influenced by the gas content of the steel itself, because of the fact that the gas can have an effect in the grain boundaries.

Dr. SWINDEN : That is a very interesting thought. As I do not subscribe to the nucleation theory, it is a particularly welcome suggestion as an alternative in explaining the experiments which were put forward from America.

Mr. J. WOOLMAN (The Brown Firth Research Laboratories, Sheffield) : My own views are in sympathy with those expressed by Mr. Allison. While I agree with Dr. Swinden that gas analysis might be most valuable and important with regard to the control of the steel-melting operation, I feel that it has a bearing on the ultimate properties of the material. Indeed, I think that what gave rise to the question of gas analysis was that steel made in different ways had different properties, although the analyses as ordinarily determined appeared to be the same. Even steels made by the same process and of the same apparent analysis frequently had different properties. These differences could not be correlated with any differences in the microstructure. To take one particular phenomenon as an illustration, it is not definitely known to this day why nickel-chromium steels behave so differently as regards their tendency to temper-brittleness. Is it a function of the gas content of the steel ? There are other problems of a similar nature, and now that the Sub-Committee have established satisfactory methods for determining the gas contents of steels, I think that they should be applied to the investigation of such problems.

Dr. SWINDE : I think that our real task now is to apply these methods, and I hope that they will be applied and tried in a wider field than that of the Members of the Sub-Committee, to see what these things mean in terms of improving our steelmaking and in throwing more light on certain anomalies which we know exist at present.

# THE TRAINING OF METALLURGISTS

## WITH SPECIAL REFERENCE TO THE IRON AND STEEL INDUSTRIES

### PREFACE.

THIS review has been prepared by authority of the Council of The Iron and Steel Institute, but it must be made clear that the Council is not committed to take action on the lines suggested and that no individual member is necessarily in favour of all the recommendations which are made.

The Council welcomes the recent action of the Advisory Council to the Department of Scientific and Industrial Research in setting up a committee to examine the supply and training of metallurgists and gladly acknowledges that this action of the Department has quickened its own interest.

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## The Training of Metallurgists

with special reference to the Iron and Steel Industries

### SUMMARY.

The supply, training and status of metallurgists have recently been examined by the Council of The Iron and Steel Institute. Steps are recommended to improve the present shortage. Education is reviewed with reference to the Government's White Paper on Educational Reconstruction. Problems of university education designed to produce both men for research and officials who will be responsible for production in industry are examined, emphasis being laid on the importance of firm grounding in the basic sciences and on early works experience; specialisation should be postponed to the post-graduate stage. Facilities for scientific and technical training for non-university men and youths require improvement, importance being attached to opportunities for completing education after entering industry. The value of works training schemes is stressed. Problems of adult education are considered including vocational and technical training for operatives. Improved status and prospects for metallurgists are recommended.

### INTRODUCTION.

METALLURGY<sup>1</sup> is one of the most important branches of applied science. It is the scientific basis on which are built the great industries which produce or use iron and steel and the various non-ferrous metals—aluminium, copper, lead, magnesium, nickel, tin, zinc, and many others. Without the development of the science of metallurgy the great engineering achievements of modern times would not be possible.

Metallurgy is, however, a relatively new branch of science. Less than a hundred years ago it had not been separated from chemistry, of which it then formed a minor part. Just as engineering has been divided into civil, mechanical, electrical and other departments, so has chemistry been divided into specialised fields, organic and inorganic. Just as proficiency in certain branches of engineering involves knowledge also of others and of physics, so proficiency in metallurgy involves knowledge of other branches of chemistry, of physics and of other kindred sciences. The study of metallurgy is no simple matter.

<sup>1</sup> The definition of metallurgy given in the Shorter Oxford English Dictionary, 2nd edition, is: "The art of working metals, comprising the separation of them from other matters in the ore, smelting and refining; often, in a narrower sense, the process of extracting metals from their ores." The common meaning of the word has, however, been extended to include, in addition to the older study of "the reduction of metals from their ores," also the study of "the nature, properties and behaviour of metals and of alloys" (see Rosenhain, "An Introduction to the Study of Physical Metallurgy," 3rd edition, p. 1 (London, 1935: Constable & Co., Ltd.)). Hence metallurgy is now usually divided into "process" and "physical" metallurgy, for descriptions of which see § 44.

Metallurgists, or men skilled in the science of metallurgy—men knowledgable in the art of working metals—are required for many purposes : For research and development; for the production of iron and steel and other metals and for working them so that they may be available in a form convenient for general use; for employment in the industries which use metals, in engineering and in factories engaged in producing all kinds of commodities, from aeroplanes or motor cars to gramophones or household utensils; for teaching others who may carry forward and increase the knowledge which they themselves possess.

The Council of The Iron and Steel Institute,<sup>2</sup> as the result of an enquiry from the Department of Scientific and Industrial Research, has recently given renewed attention to the education which should be undertaken by those who wish to become metallurgists and to the training which is desirable for those who hope to gain their livelihood in the metallurgical industries. Changes and improvements are necessary. These are required in the interests both of the men and of the industries. The Council hopes itself to take certain steps which will facilitate these changes, but much must also be done by the authorities who are primarily responsible for technical education in this country and by those whose duty it is to select and to train staff for employment in research laboratories and in factories.

The subject is of national importance. Everything possible should be done to enable the metallurgical industries of this country to hold their own in the new and difficult industrial conditions which are likely to prevail after the war. The supply, education and training of a sufficient number of metallurgists are among the most important steps which will make this possible.

#### SUPPLY OF METALLURGISTS.

1. There is little doubt that after the war British industry will be faced by a severe shortage of properly qualified metallurgists. This is due partly to the comparatively small numbers of students who take courses in this specialised branch of the applied sciences and partly to the greater proportion of trained men who will be needed.

2. A shortage in the numbers of metallurgists was apparent for some years before the war. Recurrent periods of industrial depression, often particularly severe in the iron and steel and some of the non-ferrous metals industries, drove a number of trained men into different walks of life and deterred others from studying metallurgy. The result was to increase the shortage when production improved. At present the shortage is accentuated by the calling up for military service of young men when, after an initial ex-

<sup>2</sup> Subsequently referred to as "the Institute."

perience in industry, they are just on the point of becoming really useful. There will be fewer well-trained men available after the war.

3. Attention has been drawn on numerous occasions to the smallness of many of the schools of metallurgy at universities. It was estimated that before the war there were only about forty advanced full-time students of metallurgy in universities and in colleges of university status in the United Kingdom, of whom about half were taking honours degrees.<sup>3</sup> This was about 4% of those studying chemistry. The position is similar in schools and colleges where less advanced education is given, although the numbers are greater.<sup>4</sup>

4. Increased numbers of men with technical and scientific training will undoubtedly be required in the metallurgical industries for filling managerial positions as well as for research and development. This will be the inevitable result both of a probable increase in capacity of some of the electric-steel and newer alloy industries and of the increased need for control in all metallurgical operations. Improved control has become necessary, partly because of the higher grade of product now made and partly because of the need to use modern complicated mechanised plant to full advantage. In addition, the employment in greater numbers of metallurgists who are qualified to carry out routine duties will be necessitated by the increased number of tests and analyses now required. Mechanised methods of testing are a partial solution, but so far have been unable to compete with the increase in demand. These tendencies show every sign of continuing.

5. The objective of those concerned with education in metallurgy should be to provide industry with sufficient numbers of officials with good scientific and technical qualifications. The objective of those concerned with the prosperity of the iron and steel and non-ferrous metals industries should be to use these officials to the best advantage and in sufficient numbers. Industry must not fail to help itself; metallurgists must be given the opportunity to make full and satisfactory careers. The metallurgical industries will not be able to hold their proper place in the economy of the country and of the world unless it is recognised that full use must be made of properly qualified men.

<sup>3</sup> Cf. R. S. Hutton, "The Training and Employment of Metallurgists," *Monthly Journal of The Institute of Metals*, 1937, vol. 4, part 12, p. 637. Reference to the late Professor (later Sir) H. C. H. Carpenter's paper on "Metallurgical Education of University Rank in Great Britain" ("Proceedings of the Empire Mining and Metallurgical Congress," 1924, Part V., p. 43) will show that the number of students at that time was far greater.

<sup>4</sup> As an example, it is understood that there were only about 450 entrants for the examinations of the City and Guilds of London Institute in metallurgical subjects in the summer of 1943. In this number, candidates who entered for more than one subject are counted separately in each entry. (See also Addendum for statement of City and Guilds of London Institute.)

Employees of various grades should be encouraged to attain given minimum standards, and lack of these standards should lessen the prospects of promotion.

#### RECRUITMENT FOR INDUSTRY.

6. Metallurgists are required for many purposes. These include, in addition to teaching in technical colleges and universities, processing at mines and in works engaged in the concentration and preliminary handling of ores; the conduct of operations in works essentially engaged in the smelting and manufacture of iron and steel and the non-ferrous metals; production in works engaged in engineering and in the manufacture of products involving the handling and use of metals; the development commercially of new and the improvement of existing materials; their sale and purchase; the routine inspection of materials and their analysis; and, finally, research of all kinds, whether conducted at universities, &c., or in laboratories attached to industrial companies or in establishments specially devoted to this purpose.

Different qualifications and different education and training are required by men proposing to earn their livelihood in these occupations.—

7. Boys and young men should be encouraged to study metallurgy and to enter the metallurgical industries. Attention should be drawn to the fascination of the subject and to the life-long interest of careers in these industries. Various means should be employed, including lectures for boys, the provision of better textbooks and the preparation of attractive popular boys' books. More important is the maintenance of closer contact with schools and the emphasis that should, during the course of general education, be placed on the part played by the metallurgical industries in contributing to the prosperity and well-being of the country. The most effective means lies, however, in the education of parents. They must be convinced that in making it possible for their sons to study metallurgy they are providing well for their futures; that their sons by entering the metallurgical industries will have reasonable chances to make for themselves successful and prosperous careers. In the last resort it is the prospects that matter; the final criterion must be the example of others.

8. Conditions of employment and prospects should be reviewed. Initial salaries should be adequate for the respective grades from which recruitment takes place and—even more important—there should be improved prospects of early promotion for those who show the necessary qualifications. Industry should recognise that boys and men cannot during the first years of employment earn the salaries which it is necessary to pay in order to attract those with marked ability. This is particularly the case with men whose scientific training has extended over a lengthy period so that

they enter industry at an age when they are naturally anxious to become self-supporting. Such men have frequently to compete with others who are already well established in industry as the result of several years' employment, since their scientific education has been shorter.

9. The highest positions in industry are open to those who have had a technical and scientific training, provided that they show also the other qualifications which are necessary, but the intention of industry to recruit its leaders from these ranks should be made clearer. (*See Addendum.*)

10. Employment must be provided after the war for those now serving in the Forces or in establishments engaged in war work; special facilities for technical and scientific education, or completion of education, will be necessary for those whose studies have been interrupted by the war. These measures are required both in justice to the men concerned and in the interests of industry.

This is part of a national problem,<sup>5</sup> but industry should supplement any national scheme by giving opportunities for part-time education (not excluding day-time education), by providing bursaries and by itself undertaking the training of these men.

The Institute can assist by establishing an Appointments Bureau to supplement the Central Register of the Ministry of Labour and National Service. Such an Appointments Bureau should keep in touch with the official organisations of the industry for commercial matters and for research, but can best be organised by the Institute, because it is in closer touch with the individuals who constitute its membership.

#### EDUCATION IN METALLURGY—GENERAL CONSIDERATIONS.

11. It has been announced<sup>6</sup> that it is the Government's policy to raise the minimum age for leaving school to 15, without exemptions, as soon as possible after the war and to 16 at a later date; and to make part-time education compulsory for all who leave school before 18 up to that age in a Young People's College or similar institution. "The hours of attendance . . . would be taken from the hours of employment as regulated by . . . law. . . . At first at any rate attendance would be limited to a day a week or its equivalent. But this is clearly a minimum."<sup>7</sup> The objective is

<sup>5</sup> Board of Education, "Educational Reconstruction," Cmd. 6458. London, July, 1943 : H.M. Stationery Office. § 99 : "It will also be possible . . . to provide a university education under the Government Scheme . . . for large numbers of men and women whose further education has been prevented or interrupted by war service."

<sup>6</sup> Board of Education, *loc. cit.*, § 22. For summary and discussion see Institution of Mechanical Engineers, "The White Paper on 'Educational Reconstruction' and its Impact on Training for Mechanical Engineers." London, 1943 : The Institution.

<sup>7</sup> Board of Education, *loc. cit.*, § 69.

apparently that for those between (15)16 and 18 up to half the normal working week shall be devoted to education compulsorily, in addition to voluntary attendance at evening classes.

These trends, although not necessarily the details, will probably be generally acceptable. They should result in a higher average standard of knowledge and ability being reached by recruits to industry as well as in a raising of the average age of entry into industry. The commercial and operational consequences of such changes will be severe, but are outside the scope of this review.

12. Recruitment to industry will as a result take place (*a*) from those who leave school as soon as permissible, (*b*) from those whose education is continued in the higher forms of public or secondary (including grammar and technical) schools, and (*c*) from those who proceed from school to a degree course at a university or analogous higher full-time course in a technical college.

It is important to industry to encourage scientific education among recruits from each of these categories, as well as the continuance of technical and scientific education after entering industry.

13. It is not unlikely that after the war at least one year's national service, including military service, will be compulsory for all youths, probably at the age of 18 or 19.<sup>8</sup> This would present special problems which are referred to below.

14. Specialisation at an early age is undesirable. Vocational training for those in category (*a*) above should be avoided and for those in categories (*b*) and (*c*) deferred and given less attention than education in general subjects and in the basic sciences. All recruits to industry should receive a sound general education appropriate to the age at which they leave school. Particular importance is attached to a proper knowledge of the English language and "to a clear understanding of the essential character and institutions of the society in which the students will be called on to play their part."<sup>9</sup> A knowledge of languages should not be neglected by those receiving higher education.<sup>10</sup>

15. A serious shortage of those properly qualified to teach scientific subjects at schools and universities is expected, and an immediate care of responsible authorities should be to ensure an adequate supply of properly qualified teachers. For the lower grades this can be done partly by the institution of intensive training courses and short-time refresher courses.<sup>11</sup> For the senior

<sup>8</sup> British Association, "Post-War University Education," (First) Interim Report of a Committee of the British Association, *The Advancement of Science*, 1942, vol. II., No. 7, pp. 255-260.

<sup>9</sup> Nuffield College, "Industry and Education—A Statement," p. 8. Oxford University Press. London, 1943: Humphrey Milford.

<sup>10</sup> Cf. Institute of Physics, "The Education and Training of Physicists," Section 8. May, 1943: The Institute.

<sup>11</sup> Board of Education, *loc. cit.*, § 105: "There are many men and women now serving in the Forces or elsewhere whose experience and devotion would greatly enrich the education of children. Short intensive courses of training will be provided for them."

grades a shortage is inevitable for some years until a supply of highly trained men can be provided. "We have to create the teachers who have the equipment to transform the existing educational system before we can produce far-reaching changes."<sup>12</sup> The provision of teachers should take precedence over the requirements of industry, since without them new generations cannot be given the education which is needed.

16. Revision of the salary scales of all grades of teachers is necessary if more men of sufficient ability are to be attracted into the profession. This is particularly the case in the lower grades, since the other advantages which attract a proportion of the ablest men in the country to university life, in spite of the relatively low pecuniary rewards, are less conspicuously available to them.

17. Closer contact should be maintained between industry and educational establishments. "A much closer collaboration between industry and commerce and the education service is essential if the country is to develop a national system [of technical education] and to secure a personnel with a training and knowledge adequate to the needs of the future."<sup>13</sup> Industry should assist those engaged in the teaching profession to keep abreast of modern developments by facilitating visits to works and by showing willingness to advise on text-books, curricula, &c. Refresher courses should be extended—a primary responsibility of the Board of Education. Those in industry should be invited to lecture to students more frequently than at present. In the higher grades, senior technical colleges, universities, &c., there should be an interchange of personnel—teachers being enabled to take up employment in industry and those at works to enter the teaching profession.<sup>14</sup> Educational establishments should be associated in solving the research problems of industry.

18. Taking a long view, it will be of lasting advantage to industry to assist in increasing to the highest level the qualifications of those in the teaching profession and to assist them to keep thoroughly up to date. This is of primary importance. The return in the ability of students of all standards and in contributions to research will amply repay industry for any immediate sacrifice.

19. The above views are expressed on the assumption that no university or similar institution can properly fulfil its functions unless attention is given to increasing the sum of knowledge as well as to the education of pupils. While the main attention of research

<sup>12</sup> British Association Report, *loc. cit.*, p. 259.

<sup>13</sup> Board of Education, *loc. cit.*, § 82.

<sup>14</sup> Board of Education, *loc. cit.*, § 103 : "Industry, commerce and other callings should contribute their quota to the teaching profession, and it should not be so true as it is to-day that once a teacher always a teacher." Cf. Institution of Mechanical Engineers, *loc. cit.*, Section III., § 7. "It would be of even greater value to arrange exchanges between the technical colleges in this country, the Dominions, the U.S.A., and other countries when the teaching work can be done in the language of the country."

workers at universities and other schools of metallurgy should be directed to investigations of a fundamental character, industry should encourage these men to associate themselves also with researches of industrial importance.<sup>15</sup>

20. An adequate standard of technical equipment is of only less importance than the quality of the teacher. It is vital in all higher educational establishments. Improvement is at present often an urgent necessity.<sup>16</sup> The conduct of education and research at many universities and technical colleges is severely hampered by the lack of sufficient modern apparatus, as well as by want of those workshop facilities which are habitual in industrial undertakings.

### THE UNIVERSITIES AND INDUSTRY.

21. It may be assumed that, as the result of the general educational policy of the country as at present intended, including the wide extension of bursaries provided by the State,<sup>17</sup> a higher proportion of the ablest youths will take a university or analogous course of higher education. Men with these qualifications should provide to an increasing extent the source from which industry will recruit its personnel and particularly those who will ultimately fill the highest executive positions, on the managerial as well as on the research side.

22. Nevertheless, the centres at which university or equivalent training is given in metallurgy are considered to be too numerous. A concentration of effort is desirable, and this has a bearing on the shortage, which is likely to persist for some time, in the supply of the highest grade of teachers. Some of the smaller schools could with advantage be closed.

23. The object of a university education must be to provide a wide knowledge of the basic sciences rather than to turn out specialists who can, immediately on entering industry, fill responsible positions and earn relatively high salaries.

<sup>15</sup> Cf. S. R. Humby and E. J. F. James, "Science and Education" (Cambridge University Press): "The indefensible distinction between 'pure' and 'applied' [science] has spread to the scientists themselves." See also P. Dunsheath, "Industrial Research in Great Britain: A Policy for the Future," *Journal of the Royal Society of Arts*, 1943, vol. 91, Mar. 5, p. 173.

<sup>16</sup> British Association Report, *loc. cit.*, p. 259: "Seeing that many scientific instruments and much apparatus now in use for war purposes will be of good value for university teaching and research . . . the Government . . . should agree in principle . . . to lend or give such instruments . . . to the universities."

<sup>17</sup> Board of Education, *loc. cit.*, § 98: "The path of the poor scholar to the university has been made broader and less difficult during the last twenty years. . . . None the less . . . the provision of scholarships and bursaries is still inadequate in total and uneven in its incidence."

*Entry to Universities.*

24. The general principles governing matriculation at most universities should be retained. A reasonable standard in general knowledge, languages and mathematics as well as in specific scientific subjects is desirable. At present the conditions of matriculation governing entry to British universities vary, and universities do not necessarily accept each other's matriculation examinations. The anomalies which result should cease to be possible. All British universities should agree to adopt common standards and conditions for matriculation.<sup>18</sup> This would not preclude colleges within universities from continuing to fix their own special and higher conditions of acceptance.

25. The present tendency towards specialisation in scientific subjects at schools from which the universities are recruited should be checked. An essential step in this direction is for the universities to revise their standards for scholarships.<sup>19</sup> Ability and a wide general education with a broad knowledge of scientific and kindred subjects should be given preference over a high standard of detailed knowledge of particular sciences, which is often the result only of intensive cramming. The content of scholarship examinations should be changed. "Entrance to a university should depend on the ability of the student to profit by the course and not merely on success in a competitive examination."<sup>20</sup> Examinations are necessary, but at present they not infrequently fail to achieve the purpose for which they are designed.

26. In the case of most young men it is undesirable that university education should start before the age of 18 or 19; if a year's national service is required it should be completed before they enter a university.<sup>21</sup>

<sup>18</sup> British Association Report, *loc. cit.*, p. 255: "An ever widening group of universities, including from the outset all those in the United Kingdom, should accept each others' tests of general education, so that a candidate who is qualified in this respect to enter a university in his own country or province will not have to submit to another general examination in order to enter any other university within the group." The question of compulsory Latin or Greek is dealt with by admitting the possibility of additional papers.

<sup>19</sup> Nuffield College, *loc. cit.* p. 16. Cf. Report of the Norwood Committee on "Curriculum and Examinations in Secondary Schools," pp. 111 *et seq.* (Board of Education. London, 1943: H.M. Stationery Office), for a very reasonable treatment of the subject.

<sup>20</sup> Institute of Physics, *loc. cit.*, Section 4. Cf. also British Association Report, *loc. cit.*, p. 255: "The award of entrance scholarships should depend more than at present upon a candidate's character (particularly his purposefulness, enterprise, initiative, originality) as well as upon his knowledge and intellectual qualities."

<sup>21</sup> Nuffield College, *loc. cit.*, p. 21. The British Association Report (*loc. cit.*, p. 255), in making "the 'modal' age of entry . . . not less than 19," seems to go too far.

*Importance of Experience at Works.*

27. It is widely held that on general principles a "break" is desirable between school and university. If this is agreed, part-time formal education should be continued, but work should not be directed to the requirements of a specific examination.<sup>22</sup>

The fitting in of a break in full-time formal education with a period of national service presents problems which cannot be solved until conditions after the war are known. All that can be said now is that the total period during which full-time education is interrupted, including any time compulsorily devoted to national service, should not normally be less than six months nor longer than eighteen months.

28. The greatest importance is attached to early experience at works. Boys leaving school should, whenever possible, before entering a university spend some months at a works, and industry must be willing to accept pupils in this and other categories to a far greater extent than has been the case in the past. Responsibility must be accepted for the training and well-being of these young men. The charging of fees is undesirable; rather ought some remuneration or an allowance to be paid.

29. It will depend on the form of national service required after the war whether a period spent at works can be included as part of it. "Some attempt should be made to relate such service to the intended professions of students."<sup>23</sup> This is highly desirable and need not exclude concurrent military training, to be preceded or followed by more intensive military service if necessary. Service in a Training Corps, by making possible the continuance of military training after entering a university, may enable an earlier period of military training to be reduced. Industry should inform the Government of its views on this subject.

30. Students at universities, &c., should spend part of their long vacations at works or in suitable laboratories as a necessary part of their education, and account of this obligation should be taken in the framing of examinations.

31. The Metallurgical Institutes, especially if adequately linked to the industries' central organisations for research and development, could well accept responsibility for such central direction as may be required. They would work in close touch with the

<sup>22</sup> Nuffield College, *loc. cit.*, p. 19. Institute of Physics, *loc. cit.*, Section 20. Norwood Committee, *loc. cit.*, p. 16, where a break of six months is favoured on educational grounds. Institution of Mechanical Engineers, *loc. cit.*, Section V., § 3. (See also Addendum for a reasoned view.)

<sup>23</sup> British Association Report, *loc. cit.*, p. 255. Optimism appears to lose touch with reality when the report recommends that "a year's education abroad after the age of eighteen might be accepted as one form of international service," or indeed, at the present time at least, in the report's conception of "a year of approved national or international service, whether civil or military."

industrial organisations, but details should be arranged locally between industry and the educational authorities.

#### *Undergraduate Tuition.*

32. Metallurgical courses at all universities and senior technical colleges should include both "process" and "physical" metallurgy.<sup>24</sup> Teaching, up to the taking of a degree, should be concerned with the principles of science without undue reference to specialisation in ferrous or non-ferrous metallurgy.

33. A university or analogous course designed to produce a fully qualified metallurgist will consist essentially of two periods. The first should be directed to the higher study of basic scientific subjects in a fairly wide alternative field including mathematics and the principles of engineering. This course might well be common to all schools of science and, in the case of undergraduates intending to read metallurgy, should lay special emphasis on chemistry and physics. Encouragement should be given to those contemplating a career in industry on the production side to study engineering. Little if any time at this stage need be given to metallurgy as such. The second period should be devoted to continuance of study in some of these fields and to the particular study of metallurgy.

Some time, especially during the preliminary period, ought always to be devoted to general subjects, including, for example, languages,<sup>25</sup> even though education at school is made less specialised.

34. The time spent in these two periods must necessarily vary, partly because the standard previously reached by those entering a university will always vary.

The ideal for a boy of high ability going up to a university at about 18 or 19 years of age, after having completed not less than a year's national service, is probably two years in each period.

This admittedly extends the age of formal education beyond that which is desirable or possible in many cases. There will always be men who, as the result of early development, had better enter industry a year or two earlier or who, through financial reasons, are compelled to do so. For these a year less should be required. It will depend on the standard reached before leaving school as to whether the first period can be curtailed, but the emphasis of university education up to the taking of a degree should be on the acquisition of a sound knowledge of the basic sciences rather

<sup>24</sup> General principles only are under consideration. An explanation of these terms is given in the note to § 44.

<sup>25</sup> Institute of Physics, *loc. cit.*, Section 8: "In particular, a knowledge of foreign languages is important to any physicist and for a research worker should be regarded as a normal part of his equipment." Cf. British Association Report, *loc. cit.*, p. 256: "Apart altogether from the academic study of language and literature, every university should require its students to be able to make themselves understood, by speech and writing, in some one auxiliary means of international communication."

than on the acquisition of a detailed knowledge of metallurgy or works practice.<sup>26</sup>

An extension of the tutorial or seminar systems in partial substitution for lectures is likely to prove beneficial.

35. There should be no lowering of the standard required for a degree; rather should the tendency be to raise the standard. A minimum course of three years should be required for all degree courses.<sup>27</sup>

36. A degree is evidence that a man has had a university education and has passed certain examinations. It is therefore evidence that he has reached a certain standard of attainment. The minimum standard required for a degree ought to be roughly the same at all universities, but naturally men should be encouraged, as they are now, to reach a higher level. It is impracticable and in opposition to the traditions of British universities to attempt uniformity, either of courses or of standards, nor is this customary in other countries. A wide measure of elasticity in degree courses between universities and within the same university is both unavoidable and desirable.

37. It is not within the scope of this review to consider the details of university curricula, but it is considered essential that universities should reconsider these in the spirit of the views expressed.<sup>28</sup> While attainment of a reasonable standard of general knowledge, languages and mathematics should continue to be an essential condition of matriculation (and after making full allowance for the need to avoid specialisation in the earlier stages of university education), it is undesirable that students who show aptitude in certain sciences, including metallurgy, should be delayed in making progress or even precluded from taking an honours or special degree by inability to attain an unreasonable standard of pro-

<sup>26</sup> Cf. Institute of Physics, *loc. cit.*, Section 13: ". . . a general course in science would normally be a prelude to entering the Honours School of Physics."

<sup>27</sup> Cf. Institute of Physics, *loc. cit.*, Section 11: ". . . at least three years' attendance at a university . . . should be a necessary condition for the award of a first degree." Section 14: ". . . the successful completion of such a course would in itself entitle the student to a first degree at the end of three years at a university. The majority of students, however, will come to the university so well prepared that they will be able to complete the course in two years. The student should then elect either to specialise by taking an honours physics course or to broaden his education by taking further courses for one or more years." The British Association Report, *loc. cit.*, p. 256, recommends "at least one year's residence." For a general discussion of the purpose and scope of university education see Norwood Committee, *loc. cit.*, p. 23. For the external degree of the University of London see § 66.

<sup>28</sup> Hutton, *loc. cit.*, p. 636: "With all the changes that are in progress in the scientific advance of our subject, it seems to me highly desirable that the educational curriculum should be overhauled at relatively frequent intervals." Seven years is suggested. An admirable account of curricula at the leading fourteen universities and colleges of university rank is given in Sir Harold Carpenter's paper (*loc. cit.*), as well as a history of metallurgical teaching in this country.

ficiency in other subjects such as higher mathematics or foreign languages. The danger of specialisation after matriculation can be sufficiently avoided by extending the choice of subjects ancillary to those which form the main interest of the student.<sup>29</sup>

38. Similarly, without in any way contradicting the views expressed on the inappropriateness of universities attempting vocational training, some use of actual plant in tuition and some acquaintance with current processes of manufacture should form a part of every university course.<sup>30</sup> Periods spent at works during vacation will enable the keen student to arrive at a true appreciation of the relation of theoretical and laboratory tuition to works conditions, but this will be facilitated by that personal contact with the problems of production which can be obtained only from personal manipulation of plant and participation in the processes of manufacture, even if these are on the very reduced scale which alone can normally be provided in educational establishments.

39. It is a matter of relatively little importance whether more universities adopt the procedure of granting a special degree in metallurgy or whether university courses in metallurgy result in the obtaining of a degree in science or in arts.

#### *Post-Graduate Education.*

40. Improved facilities for post-graduate tuition are of great importance for training men of marked ability or those who are anxious to acquire detailed knowledge of a particular branch of metallurgy. The objections to specialisation previously mentioned do not apply at this stage. In fact intensive study, including participation in solving research problems of current interest to industry, should be encouraged.<sup>31</sup>

41. Universities might with advantage concentrate for purposes of post-graduate teaching on certain aspects of scientific work related to metallurgy. Such specialisation is indeed the requisite of full participation in the research activities of the country; it should normally bear a relation to the requirements of industry in the district.

Post-graduate students intending to enter a particular branch of industry or to embark on a selected line of research should be encouraged to complete their education at a university where appropriate fields of study have been developed. Whenever possible it is desirable that a post-graduate course should be taken at a different British university or at one in a foreign country.

<sup>29</sup> For further discussion and recommendations in favour of honours and pass schools in "Philosophy, Natural and Social," see British Association Report, *loc. cit.*, p. 258.

<sup>30</sup> British Association Report, *loc. cit.*, p. 258: "It is, however, essential that . . . there should be opportunity for observational work in the field."

<sup>31</sup> The suggestion of the British Association Report, *loc. cit.*, p. 258, has already been quoted. See note to section 38 above.

42. Universities should adopt a roughly common standard for the granting of a Ph.D. degree. "It is most undesirable for graduates who do not show real promise for scientific research to remain at the university simply in order, through a single piece of research work, to obtain a Ph.D. degree. Research or other post-graduate work should, it is felt, be used to complete the intellectual training of the most suitable men, and the Ph.D. degree should be regarded as a possible result, but not as the purpose, of such work."<sup>32</sup>

43. Universities might attempt to a far greater extent than is at present the case to cater for the legitimate requirements of industry by providing special post-graduate courses. These would include short intensive instruction in special branches of industry, not excluding practical courses amounting almost to an apprenticeship. Such courses would include those designed explicitly for graduates whose main interest lies in particular spheres of works operation.<sup>33</sup> The Metallurgical Institutes are well qualified to advise universities on the scope of such courses.

#### *Process and Physical Metallurgy.*

44. Among the subjects in which universities have specialised for purposes of research and post-graduate teaching are particular aspects of "process" or "physical" metallurgy. In this connection it is relevant to point out that the definitions of these terms vary. By "process metallurgy" is usually meant "the study of the occurrence and mining of ores, the principles of processing and concentration, smelting and all stages of manufacture up to the ingot or equivalent." Sometimes, however, the meaning is restricted to "the extraction of metal from a dressed or concentrated ore or from scrap and residues," thus excluding the initial preparation of ores. The term is used here in its wider meaning.

By "physical metallurgy" is meant "the study and treatment of metals after they have been produced as metals in ingot or other form."<sup>34</sup>

<sup>32</sup> Institute of Metals Report, May, 1943 (unpublished).

<sup>33</sup> Cf. Institute of Physics, *loc. cit.*, Sections 16 and 17: "There is evidence of a demand for short post-graduate courses in certain highly specialised branches"; and "The Board of the Institute should take the initiative in making arrangements for short advanced courses both on the theoretical and experimental side."

<sup>34</sup> Cf. Institute of Metals Report, *loc. cit.* The wider definition of "process metallurgy" is required when reference is made to the iron and steel industries, in which the smelting of the ores to produce iron is commonly carried out as an integral part of operations which at a later stage, by further treatment of the molten iron, result in the production of steel. In the non-ferrous metals industries the more restricted definition is often convenient, since the initial processing of ores is usually conducted at the mines or at separate plants. The meaning of "physical metallurgy" can best be illustrated by reference to the iron and steel industry, where the production of both pig iron and steel may result in confusion; in the case of this industry "physical metallurgy" means "the study of the product, including pig iron, steel ingots and castings, and the study of processes of manufacture later than smelting."

45. The importance of developing the study and teaching of process metallurgy is emphasised, since present facilities are considered inadequate. This branch of metallurgy is likely to be of increased importance in developing national and imperial resources without infringing on the legitimate aspirations of other nations of the Empire to develop their own schools. The training of men, including those from overseas, whose lives will be devoted to the development of the mineral resources of the world is a matter of national importance.

46. This aspect of the question has an important bearing not only on the provision of suitable careers for young men from this country and the Empire but also on establishing British influence in foreign countries. "One-way traffic is not enough." Encouragement should be given to men from other countries to obtain technical training in all branches of metallurgy at British universities and technical colleges. Foreign countries should be brought to look to Great Britain for inspiration in developing their resources and for supplementing their own technically trained men by the employment of highly qualified British specialists. All too often in the past have foreign countries obtained the assistance they needed from America or the Continent.<sup>35</sup>

#### *Equipment.*

47. The provision of up-to-date equipment at universities is a matter of urgent necessity. There is much to be said for the closer connection between industry in a particular district and the university located there resulting in industry supplementing the technical equipment of the local university by providing or lending plant, instruments and specimens which universities cannot or do not obtain from their own resources. This is not solely, nor perhaps primarily, a question of expense; without close connection with industry universities are unable to judge what equipment is required, nor to appreciate what renovations and renewals are indispensable. Nevertheless, substantial initial capital expenditure is undoubtedly necessary in a number of cases.<sup>36</sup>

#### *Training of Graduates by Industry.*

48. With some notable exceptions the present arrangements for placing students in industry are not satisfactory; University Appointments Boards appear all too often to be unable to appreciate the qualifications which industry considers essential. "Industry has a right to claim a higher proportion of the best men from the universities than it has been getting in the past. . . .

<sup>35</sup> British Association Report, *loc. cit.*, p. 257. Free board, lodging and tuition and free passages to outgoing graduates are recommended on the example of American university practice.

<sup>36</sup> Institution of Electrical Engineers, "The Organisation of Post-War Electrical Research," p. 6. London, 1943: The Institution.

The fundamental remedy is to be found, not in any kind of formal register, but in much closer contact between the teaching staffs of universities and those responsible for the recruitment of the higher personnel of industry."<sup>37</sup> The Institute should play its proper part in the placing of recruits in industry.

49. It is apparent that young men who have graduated will normally not enter industry before the age of 21 and may often be considerably older. These men will have secured a good background of general education and have devoted a number of years to the study of the basic sciences. They will have spent at least one or two years studying metallurgy and have spent a substantial period at works. In addition they will have had an opportunity to acquire that facility for leadership and social adaptability which is, or ought to be,<sup>38</sup> among the major objectives of a university education. Sympathy should be shown by employers to the natural desire of many young men of this age to be quit of tuition and rapidly to fill positions where they will have responsibility and become financially self-supporting. Nevertheless, departmental responsibility should whenever possible be deferred until after vocational training over a period varying from some months to a couple of years.

50. In large concerns there is relatively little difficulty in arranging for graduates to spend time in various departments or works. The wider adoption of training schemes operated by a limited number of companies is highly desirable. They are invaluable in assisting both the company and the employee to decide the activity which is likely to be most congenial and suitable.

Although there is greater difficulty in arranging for such a probationary period in smaller companies, it should become the general rule. Groups of smaller companies in a district could combine to operate a joint scheme. Arrangements could no doubt also frequently be made for larger companies to accept such entrants into industry for a period in their works at the request of the smaller companies by whom they are employed. Periods of training at central research establishments could be arranged. Use could be made to some extent of interchange between works and offices, since it is imperative that responsible technical officials should acquire a reasonably good knowledge of office routine, accounting, &c. These latter expedients, however, have the drawback that they do not make possible that further intimate contact, supplementing the experience already obtained during vacations, with works conditions and workmen which is desirable for all who propose to take up an industrial career.

51. It may be assumed that, while those who show special

<sup>37</sup> Nuffield College, *loc. cit.*, pp. 24, 25. See also Institute of Physics, *loc. cit.*, Section 21.

<sup>38</sup> British Association Report, *loc. cit.*, p. 257: "Little is done to ensure that every undergraduate is faced by the need for working out a philosophy of life."

adaptability for research of the highest grade will tend to take the fullest honours courses and afterwards to continue with post-graduate studies, many men who are more attracted to managerial positions will leave the universities at the earliest opportunity after graduating; but any tendency to suggest that those who prefer this type of career should always enter industry at an earlier age is to be deprecated as much as a suggestion that a lower standard of ability or attainment is necessarily sufficient. Encouragement should be given to all who can benefit from it to continue their studies.

Not unimportant factors in such later education are those which result almost automatically from the undertaking of a particular piece of research or works investigation; from the writing of papers for scientific or technical societies; from contributing to the discussions at meetings; from teaching at technical colleges and from competition for prizes. Companies might well encourage special work and supplement the activities of the Institutes by offering premiums and advanced promotion to those who distinguish themselves—subject to the overriding necessity that they have the other qualifications which are of paramount importance to the holders of responsible positions in industry. Resumption of formal education for limited periods and opportunities for taking refresher courses at universities should not be ruled out.

52. Past experience has shown that many men whose education has been primarily directed to acquiring proficiency in physics and chemistry have, after entering industry, become metallurgists whose knowledge and whose value to industry are in no way second to those of men whose early education has been more specifically metallurgical. The success of these men indeed illustrates the value of sound scientific attainment over early specialisation. Nevertheless, the tendency of the views expressed is undoubtedly that students should be encouraged to take a degree course in metallurgy. This is desirable both because better grounding is thus obtained and because the scope of the science has increased far more during the last few decades than is generally appreciated. The metallurgist "has a vastly greater field to cover and the days are past when a chemist could switch over to metallurgy without taking quite extensive supplementary courses of instruction in the subject."<sup>39</sup> In the case of selected men who are able and willing to spend the necessary time, graduation in physics or chemistry may suitably be followed by two years' post-graduate study of metallurgy.

All arrangements in education should be flexible. These special cases are exceptions to the normal procedure and do not invalidate its general applicability.

<sup>39</sup> R. S. Hutton, *loc. cit.*, p. 634. See also p. 638: "Until recently, a good chemist or engineer could rapidly adapt himself to become a competent metallurgist, but . . . this is becoming much less easy, on account of the rapid growth of its specialised branches."

## EDUCATION IN METALLURGY BELOW UNIVERSITY STANDARD.

53. Most recruits to industry will necessarily continue to come direct from school, and of these a majority, for many years at least, will still enter employment at the minimum leaving age or shortly after from secondary schools—grammar, modern and technical.<sup>40</sup>

54. The same general principles apply as in the case of those whose whole-time education has been continued to a later age. The chief differences in treatment necessary are that greater encouragement and greater facilities for part-time technical and scientific education (including part-time day education) after beginning work are required, and that improved opportunities must be provided for those who show special ability or character to win generally recognised qualifications and to rise to positions of responsibility in their profession.

It must not be forgotten that it is from this category that a large proportion of the most useful men in managerial positions in the metallurgical industries is at present drawn. Some of these entered industry at the earliest age; a few have risen to positions of the highest responsibility. From the ranks of these boys industry can in future by wise treatment obtain many of the men it needs.

55. It should be frankly recognised that those entering industry at the minimum school-leaving age or soon after will have no knowledge of metallurgy and only a rudimentary knowledge of the basic sciences. The most that can be hoped for as the result of the looked-for improvement in elementary education—and this is by far the most urgent of all educational problems in England and Wales to-day—is that after attending a primary and secondary school a pupil will have obtained a sound general education up to a reasonable standard.<sup>41</sup>

56. The technical and scientific education of these lads must therefore be undertaken after they have entered industry. It has been announced that, subject to Parliamentary approval, attendance at a Young People's College or equivalent institution, including works schools, will be compulsory up to the age of 18 for all whose full-time education has ceased at an earlier age. Beginning with one day a week, it is proposed that compulsory attendance shall ultimately be extended to half the normal working week. In the education to be provided "essential elements will be training in clarity of expression and in the understanding of the written and spoken

<sup>40</sup> For new terminology see Board of Education, *loc. cit.*, § 31: "It would be wrong to suppose that they will necessarily remain separate and apart." For a general discussion see Institution of Mechanical Engineers, *loc. cit.*, Section V.

<sup>41</sup> Nuffield College, *loc. cit.*, pp. 8, 9. Cf. Norwood Committee, *loc. cit.*, p. 20: ". . . for in our view the technical school should give a general education." This does not, of course, mean that boys should not be encouraged in school as well as in their spare time to become skilled in handicrafts, &c.; the contrary is the case.

word, together with some education in the broad meaning of citizenship," but "when basic requirements have been met, the remaining hours may well be devoted to a variety of subjects" of value to the pupils, including in all appropriate cases "technical or vocational education related to their employment."<sup>42</sup>

57. The work of the Young People's Colleges may therefore be expected to supplement, and eventually perhaps to supersede, on a compulsory basis work which is now being done by voluntary attendance at evening classes.

Emphasis is laid on the necessity of some formal tuition during normal working hours, because tuition by evening classes alone suffers from the serious drawback that pupils are often tired after the day's work and that those who complete courses—a relatively small proportion of the entrants—not infrequently suffer from "an impoverishment of initiative and intellectual quality at a period of life critical for the full development of the powers and capacities of the individual."<sup>43</sup>

Nevertheless, it is apparent that for some years at least the time available at compulsory day-time classes will be totally insufficient for the technical training which is necessary. Evening classes do provide invaluable opportunities for improving knowledge and, it is clear, must continue to play a part in the advance of technical and scientific education.

58. Part-time education should provide facilities which make it possible for pupils ultimately to attain a standard in a particular subject comparable to that obtained by study at a university, even though general education need not necessarily be so wide as to meet the requirements of university matriculation examinations; it should be possible to win qualifications which demonstrate the attainment of this standard. But it is just as important that opportunities should also be provided for those who have less high academic ambitions to obtain a sound technical and scientific knowledge of the processes of the industries in which they are employed and to obtain that training in craftsmanship which will provide them with a sounder understanding of, and greater interest in, their work and enable them to do it better. This is a duty which the works schools<sup>44</sup> are particularly suited to undertake, but it should certainly not be excluded from the functions of technical colleges.

59. Facilities for part-time education in metallurgy vary throughout the country, but on the whole compare unfavourably with those available to students of chemistry, engineering,

<sup>42</sup> Board of Education, *loc. cit.*, §§ 67–69, 73, 74. Cf. also Norwood Committee, *loc. cit.*, p. 22.

<sup>43</sup> Nuffield College, *loc. cit.*, p. 13.

<sup>44</sup> Cf. the instruction of foundry apprentices by skilled men in works schools organised in a bay of the foundry by certain large companies. Board of Education, "Report of H.M. Inspector on Education in Relation to Foundry Work," Section 5. London, 1924: H.M. Stationery Office.

physics and electricity. The equipment of some technical colleges leaves much to be desired.<sup>45</sup> Curricula of courses in metallurgy are not always appropriate to local requirements or, if adapted specifically to meet the needs of industry in the district, are not built up on a sufficiently broad basis of general science and thus fail to provide adequate opportunities for pupils to win qualifications which are recognised nationally.

*National Certificates in Metallurgy.*

60. It has been suggested that the institution of National Certificates in Metallurgy would provide objectives at which those continuing their education by attendance at part-time or at evening classes could aim and that a desirable result would be to produce a levelling-up of the standard of part-time education throughout the country.

61. At present, in the absence of National Certificates in Metallurgy, many pupils study engineering and chemistry with the object of obtaining National Certificates in these subjects and of then proceeding to membership of the institutions concerned, while technical colleges, in an endeavour to meet the needs of those engaged in the local metallurgical industries, extend their syllabuses by the inclusion of courses which are definitely metallurgical in character but which do not properly belong. The student who is interested in metallurgy must often give undue attention to other subjects if he wishes to win a nationally recognised qualification, and his training and outlook are biased accordingly.

62. National Certificates are of two grades. The Ordinary Certificate is awarded after a three years' course of study adapted to the needs of students between the ages of 16 to 19. Failing a continuous full-time education up to 16, the student is required to take a part-time preparatory course.

The Higher Certificate is awarded after a further two years' course of study for students who have obtained the Ordinary National Certificate or are otherwise suitably qualified. The general level of work is of a standard comparable with that of a final university degree, although the range of work is not usually as extensive.

63. The effect of a year's national service in interrupting this course of study is part of a problem common to all industries for which such schemes are operated and need not be further considered here, but it is apparent that the age of service or the course of instruction should be adapted to make the break come after the winning of an Ordinary Certificate and thus to place part-time pupils

<sup>45</sup> Board of Education, Cmd. 6458, *loc. cit.*, § 79: "The standards of buildings and equipment in use have often been deplorably low." They compare unfavourably with those in countries which are "our competitors in the world markets." And § 80: "A programme of capital expenditure of some £12,000,000 was contemplated before the war"—the post-war cost will be higher, but must be incurred.

in the same position as those who have remained at school to a later age.

64. The work of the Department of Technology of the City and Guilds of London Institute has been invaluable in encouraging students. Essentially an external examining body, syllabuses are framed by an advisory committee, on which the Board of Education, teachers and the Metallurgical Institutes are represented. Attendance at prescribed classes is not necessary, but many students at technical colleges are now in fact prepared for the Ordinary or the Full Technological Certificates. Attainment of the latter involves a reasonably comprehensive knowledge of scientific subjects, as well as of "the principles and practices of metallurgical operations." The examinations of the City and Guilds should be incorporated into any scheme for the award of National Certificates in Metallurgy.

#### *Facilities for Higher Education.*

65. Many of the most valuable recruits to industry are youths who have spent some years after attaining the minimum school-leaving age at a public or secondary school (including the grammar and technical schools) but have not gone on to a university. "The adolescent who leaves school to enter industry at 17 or 18 should have received, up to the level appropriate to his age, a rounded education and not part of an education designed for persons whose full-time education is to continue for some years more."<sup>46</sup> These lads will in many cases, as part of a good general education, have obtained a grounding in the principles of the basic sciences, of engineering and of mathematics, but will not normally have secured much, if any, knowledge of metallurgy or works processes. They will be able to take their proper places in the scheme of part-time education which has been outlined.

66. Facilities provided by the University of London enable advanced students working in their spare time to take an external degree, *i.e.*, that of B.Sc. in Engineering in Metallurgy. The standard is fully equal to that required for graduation by those who attend full-time courses at other universities. Although comparatively few candidates can proceed to a degree as the result of continued part-time study over a number of years, the possibility is valuable for those who are unable to attend a university in the ordinary way. The facilities should be continued, even though there does not appear to be any need for the institution of external degrees elsewhere, but their value would be increased if the recommendation previously made were adopted and the choice of subjects required for matriculation standardised throughout the country.

<sup>46</sup> Nuffield College, *loc. cit.*, p. 16. The paragraph continues : "To secure this, it is necessary to release the schools from thrall to an examination system conceived too much under university needs, or rather from a standard which regards the school primarily as a place of preparation for university work." (For City and Guilds of London Institute, see Addendum.)

Technical colleges, for which the Sir John Cass Technical Institute may serve as an example, provide tuition in metallurgy, mostly by evening classes, which assists part-time students to qualify for a degree and, in a few cases, if authorised by the university, subsequently for a Ph.D.

67. Certain senior technical colleges provide facilities for the study of metallurgy which are fully equal to university standing. "The Royal School of Mines is the pioneer of metallurgical education in this country. It was founded in 1851 as a direct result of the Great Exhibition,"<sup>47</sup> and no other school of metallurgy of university standing existed for over thirty years until the foundation of the Sheffield Technical School (now the Faculty of Metallurgy of the University of Sheffield) in 1884. The Royal School of Mines is one of the three colleges which have federated into the Imperial College of Science and Technology. This college has been established as a school, but not an incorporated college, of the University of London. Provided, however, that they have matriculated, students can sit for the B.Sc. degree of London University by taking the appropriate examinations, as well as for the Associateship of the Royal School of Mines. Non-matriculated students can obtain the Associateship, the value of which is widely recognised.

68. At a few other universities and colleges of university standard (Sheffield, Manchester, Glasgow) the opportunity is provided for obtaining an Associateship, the standard being comparable to that of a pass degree in metallurgy and kindred subjects, but, as matriculation is not required, those who work for it may have a lower standard of attainment in subjects other than science (*e.g.*, mathematics or foreign languages).

This qualification has secured wide acceptance by industry in the districts concerned, even if it is less generally recognised outside.

The regulations vary. Full-time study may be essential. Generally speaking, however, three years' full-time day study or five years' attendance at evening classes is required. A serious objection in the latter case is that those who are in full-time employment find the strain of completing the courses severe and only a small proportion succeed in doing so. Nevertheless, it is desirable that similar facilities should be made available also in other industrial centres.

### *The Responsibility of Industry.*

69. It is apparent that the part which industry must play in encouraging part-time education is of paramount importance.<sup>48</sup>

<sup>47</sup> Sir Harold Carpenter, *loc. cit.*, p. 49.

<sup>48</sup> Board of Education, *loc. cit.*, § 81 : "The vocational training that has come into being within the system of public education has in the main not come in respect to any demand from industry or commerce, but has depended on the enterprise and tenacity of individual students anxious to equip themselves more fully to advance in life."

Apart from statutory requirements, young employees should be encouraged to undertake further study by the granting of reasonable facilities to attend classes during working hours. "Release should be made easy both for day-time attendance at appropriate classes and for private study; and, wherever possible, a period of entire release prior to critical examinations should be arranged."<sup>49</sup> Close co-operation with technical colleges is desirable. Advice should be readily sought and freely given. Those in responsible positions in industry should join in teaching at night classes. Merit in part-time study by junior employees should be recognised by their employers. Assistance should be given in the payment of fees when tuition is not free.

70. Works training and apprenticeship schemes are, if possible, of even greater importance in improving the scientific and technical education of younger entrants into industry than of those whose full-time education has been prolonged to a later age.

A number of these schemes are already in existence and they vary considerably in procedure and facilities. In one of the most successful, apprentices are accepted between the ages of 16½ and 18½; they are transferred at regular intervals from one department or works to another, and it is a condition that they shall take certain prescribed evening classes; the total period of training is four years. In another case employees of 17–18 years of age are selected by the management on the basis of progress at the evening classes of the local technical college and utility in the works. Six months' full-time study at the technical college during the winter is alternated with six months' employment at the works during the summer over a total period of three years; wages are paid during the whole of this training.

In most successful schemes the progress made by apprentices is supervised by specially detailed officials; wages are paid and merit is rewarded by bonuses above the prescribed minimum scale.

A wide extension of schemes on existing lines or on other lines to be developed locally should not be delayed by the difficulty of deciding which type of scheme is best. Indeed uniformity, beloved of officialdom, is the foe of education. Success depends on individual and local effort.

71. The part which works schools and apprenticeship training schools within the works of larger firms can play in this general scheme of education should not be ignored. They can be of exceptional value in fostering understanding of the processes of manufacture in which the pupils are engaged. Nevertheless, it is preferable that their work should in all the higher ranges be accompanied by attendance at central technical colleges where tuition in engineering and science, as well as in the principles underlying the processes of manufacture, can generally be provided on a wider basis.

<sup>49</sup> Nuffield College, *loc. cit.*, p. 17.

## ADULT EDUCATION.

72. Boys and youths will, if the proposals discussed in this review are adopted, have considerably better opportunities for perfecting their technical and scientific education; they should become better men. The full advantages to industry can, however, only be obtained if the scheme for technical and scientific education with particular reference to metallurgy and kindred sciences is comprehensive. The later education of employees must not be neglected.

*For Managers and other Staff.*

73. The provision of opportunity for improving their knowledge and bringing it up to date is not a difficult problem in the case of those who in early manhood have attained a standard roughly equivalent to that of a degree.

Universities and analogous institutions should provide refresher courses and short special courses in which intensive tuition in some special subject is given.

74. These courses might well include lectures, coaching and laboratory or workshop tuition in special aspects of metallurgy, chemistry, physics or engineering of application to industry, but not perhaps normally covered by formal education or only recently developed. Other courses might be arranged in higher mathematics as applicable to works practice and in the use of statistical methods, or facilities might be provided for the detailed study of highly complex works and research problems. In addition, courses with a more limited practical or theoretical aim would be useful.

75. Such courses should normally be evening classes at universities or institutions in industrial centres, but it is essential that these establishments should provide special facilities to meet the natural reluctance of men who have attained positions of some responsibility to compete with their juniors.

It is desirable also that universities with special residential facilities should provide short courses, varying from a few days to a week or fortnight, which could be attended by officials at works, including those in senior positions, and by those employed in research laboratories. The value of these is likely to be great, and companies should be prepared to give reasonable facilities to members of their technical and scientific staffs to attend without encroaching on their holidays.

76. The provision of technical courses for commercial officials is outside the scope of this review, but occasional courses, perhaps preferably residential, where directors and higher executives who have not had earlier opportunities could obtain a general view of the scientific principles on which their industry is based as well as of the various technical processes involved, are likely to be popular.

77. The interchange of staffs between industry and research associations, universities and other teaching establishments should be made easier in the interests of all parties. Many works officials would benefit by a period spent in research or in teaching, while it is at least equally important that those who prefer a career in the comparatively sheltered atmosphere of the laboratory should obtain occasional personal experience of the actual processes in which their theoretical deductions and fundamental explorations are applied. The importance of this to teachers has already been emphasised.

78. The interchange of staffs would be made much easier if there were adjustments in "the different salary structures of academic and industrial life."<sup>50</sup> The arranging of greater flexibility in pension schemes is part of the same problem.

79. An extension is desirable of the present system by which scholarships and prizes can be won by those who present papers of merit to the Institute and other societies, or who show evidence of capacity to conduct special investigations, with profit to themselves and to their industry. Travelling scholarships should be provided to enable the best men to study special problems in other countries and to widen their experience. The practice extensively exercised by industrial concerns before the war of sending members of their staffs to other parts of Europe or the world is highly beneficial. It could with advantage be extended by making it possible for technical officials to spend more time on these visits and even to work for short periods in foreign establishments.

#### *For Foremen and Workmen.*

80. The problem of providing suitable opportunities for adult education for workmen and those who have not in earlier life reached a relatively high standard is more difficult but not less important. "We are concerned at least as much with the quality, well-being and happiness of the main body of the manual workers in industry as with the education of those who fill the higher positions in its service."<sup>51</sup>

81. Two somewhat different needs must be filled. The first of these is to provide opportunities for those with special qualities of character, intelligence, ambition and powers of leadership—qualities enhanced by experience and the successful operation of industrial processes—to obtain that wider education which will make them capable of filling positions of greater responsibility.

<sup>50</sup> Nuffield College, *loc. cit.*, p. 23.

<sup>51</sup> Nuffield College, *loc. cit.*, p. 28. The paragraph continues: "No success in recruiting a skilled and intelligent body of men for the higher posts will avail us unless at the same time everything possible is done to achieve the best possible quality in the rank and file." See Institution of Mechanical Engineers, *loc. cit.*, Sections VI.-VIII., for an interesting discussion on practical training.

This can be done by means of part-time education, mostly at evening classes, as already described. Greater encouragement on the side of employers is required and improved facilities, especially in the provision of special classes at technical colleges. No man likes to go to school with his son.<sup>52</sup>

82. The greatest need in adult education is, however, the provision of opportunities for the ordinary intelligent workman to obtain some knowledge of the principles of science and engineering and the theory behind processes which he employs in his work. Such men commonly have exceptional personal knowledge of processes and materials or a fine manipulative skill, on which in the last resort the whole structure of manufacture, however mechanised, is dependent, but there comes a time when neither personal skill, nor experience, nor knowledge gained from colleagues can provide explanations of what is happening and why.

83. The importance of vocational training should not be forgotten. Industry, as well as educational establishments, should provide increased facilities, not necessarily solely outside ordinary working hours.<sup>53</sup> Specialised schools have proved their value, and, while so far strictly limited in number, the idea might well be extended.<sup>54</sup>

84. At large works special evening classes for these men are undoubtedly of the greatest advantage. They obviate the necessity of a special journey to some perhaps rather grandiose centre of education and they enable men to study in company with their colleagues. Groups of smaller works could join more frequently in providing similar facilities.

85. An outstanding success has distinguished the educational efforts of the Sheffield Trades Technical Societies. This success has been due largely to the fact that the movement is truly co-operative and democratic in spirit and constitution.

The Sheffield Trades Technical Societies have developed from three societies with 400 members in 1918 to sixteen societies with a membership of over 3,500 in 1939. The affairs of each individual

<sup>52</sup> But compare the wide adoption of adult education in the U.S.S.R.; see John Scott, "Behind the Urals," pp. 39, 94, 168 (London, 1943: Martin Secker and Warburg, Ltd.). For a general discussion and review of existing organisations for adult education, including the Workers' Educational Association, see Board of Education, *loc. cit.*, §§ 85-88.

<sup>53</sup> See "A National Policy in Industry," p. 10 (London, 1942: Thomson McLintock & Co.): "We consider that industry should give much more thought to schemes for industrial and vocational education, training and promotion, so that every employee with the requisite capacity may be able to fit himself for higher responsibilities." (*See also Addendum.*)

<sup>54</sup> Cf. the "British Foundry School" organised by the British Cast Iron Research Association. The course was residential and took a year; fees and salaries were paid by the employer; only men who were already employed in industry and who had adequate practical training were accepted; the object of the course was to turn out men who were "mixtures of metallurgist, engineer and foundry technologist." The course was incorporated into works training schemes by a number of companies.

society are conducted by its own Council, but matters of interest to more than one society are conducted by an Executive Council on which each member society is represented. The Chairman and Vice-Chairman are representatives of the University. The societies provide a medium through which those engaged in the various industries of the city may come into contact and co-operate with the University. Extensive lecture courses are provided by the latter "to enable workers to study the commercial and technical side of their work and to receive the latest scientific information which may be applied to their trade." Fees are usually at the rate of 2s. 6d. for a course of six lectures. Facilities are provided for lectures, discussions, works visits and for assistance in technical problems. Members are encouraged to write articles and to compete for prizes. Exhibitions of workmanship and of technical films are arranged, and encouragement is given to meetings for social purposes. The subscription is 2s. a year.

New branches might be inaugurated in other large manufacturing cities.<sup>55</sup> This should be facilitated by the recent registration of the National Trades Technical Societies in which the Sheffield Societies are now incorporated to form the Sheffield Section.

#### METALLURGICAL EDUCATION FOR WOMEN.

86. The employment of women in the metallurgical industries raises many industrial, social and perhaps particularly political questions. Educational problems are, however, few. Most of what has been written applies equally to the education and training of women as of men; to quote the common legal phrase "words importing males include females." The skill with which women can carry out many of the duties normally undertaken by men cannot be questioned, and this skill is not confined to analytical and similar laboratory work, but has been proved in many of the relatively heavy duties of actual production. Should the employment of women in the metallurgical industries and in laboratories remain more common than was the case before the war facilities for their education would have to be provided on lines comparable to those for boys and men. In the later stages of education, courses should be open to both.

#### QUALIFICATIONS FOR METALLURGISTS.

87. The scheme of education which has been outlined should result in many more men who are employed in the iron and steel

<sup>55</sup> Cf. also the People's High Schools of Denmark. Residential colleges, privately owned but subsidised by the State, give five months' technical training in agriculture during the winter, and about one-third of the agricultural population of Denmark passes through these schools. The idea might well be adapted to the requirements of industrial workers. British Association, "Post-War University Education," Third Interim Report.

or non-ferrous metals industries obtaining a reasonably good knowledge of the scientific principles underlying the operations which they carry out, as well as in managers and others in responsible positions being drawn more extensively from those whose education and training have enabled them to acquire the knowledge and experience which are requisite. The benefit to industry can scarcely be doubted.

88. The improved facilities for education and the greater encouragement to enter the metallurgical industries which have been suggested should result in more boys and men of first-class ability studying metallurgy. Preference will, however, probably continue to be given by students, parents and teachers to chemistry and the various branches of engineering as long as those who reach a given standard in these subjects are able to obtain nationally recognised qualifications while those who have specialised in metallurgy are unable to produce similar evidence of attainment of a comparable standard of efficiency. It is the praiseworthy objective of many of the better students of chemistry and engineering to gain admittance to associate membership, and later to full membership, of the Royal Institute of Chemistry and the Institutions of Civil or Mechanical Engineers (to take three examples only), while other institutions provide similar facilities for electrical engineers, naval architects, mining engineers and other specialists. These institutions, membership of which is obtainable only as the result of the production of evidence that the candidate possesses given qualifications, usually of a high standard, have done invaluable service in raising the quality and improving the status of the professions concerned.

Metallurgists, except in so far as the Institution of Mining and Metallurgy caters for process metallurgists, have no similar prospects. Those who wish to win nationally recognised qualifications are compelled to join institutions whose primary interest is in other subjects. The result has operated disadvantageously to metallurgy and metallurgists.

89. The reason for this somewhat anomalous state of affairs is simple. When The Iron and Steel Institute was founded in 1869 metallurgy as one of the separate applied sciences did not exist—it was simply a branch of inorganic chemistry. Even in 1908, when The Institute of Metals was founded to provide comparable facilities for those whose major interest lay in the non-ferrous metals, sufficient progress had not been made to justify election to membership only on the production of evidence of technical qualifications. Progress in metallurgy during the last thirty-five years has, however, been so great that this position might well be reconsidered.

90. There are compelling reasons why membership of The Iron and Steel Institute should not be confined to qualified metallurgists. The primary duty of the Institute is to provide facilities for dis-

cussion and publication as well as to encourage research by those employed in the industries which manufacture and work iron and steel. These industries necessarily employ many engineers, physicists and other technicians as well as professional metallurgists; they need the services of specialists in refractories and fuel, statisticians and others. All these must to some degree specialise in the application of their fundamental training to the conditions of the industries in which they serve; all should obtain benefit from membership of the Institute and be equally eligible to become members. To confine membership to professional metallurgists as the result of demanding evidence of qualification would be to restrict its activities in a way which would be harmful. The desire of metallurgists for national recognition might well be met in other ways.

More detailed discussion of this subject is outside the scope of this review. It may be said, however, that it is receiving earnest consideration from those whose responsibility it is.

#### CONCLUSION.

91. The metallurgical industries look forward with optimism to a period of considerable prosperity after the war. Their confidence is justified by the vital part which these industries must necessarily continue to play in the periods of reconstruction and after if this country is not to forfeit the fruits of victory—a victory which would not be possible without their whole-hearted collaboration.

Metallurgists will be responsible for much of the work of these industries; their help will be essential in increasing the efficiency in production as well as in developing the fundamental researches on which improved qualities and new materials are ultimately dependent. Without the science of metallurgy there can be no metallurgical industry.

It will be the privilege of metallurgists to help in this work, but it is the responsibility of the Government, the Institutes, those concerned with education and of industry itself to see that those facilities for education and training are provided which will ensure an adequate supply of qualified metallurgists.

#### ADDENDUM.

Reference should be made also to the valuable statement on Higher Technical Education prepared by Professor R. S. Hutton, M.A., D.Sc., for the City and Guilds of London Institute, and the attached statement of the Council (November, 1943). Note particularly :

*Page 7.—“... the importance of improved technical efficiency, based on improved education, for the re-establishment and increase of our export trade.”*

*Page 10.—“To-day, of course, British industry is employing increasing numbers of university graduates in research departments, and in chemical control and mechanical testing laboratories.*

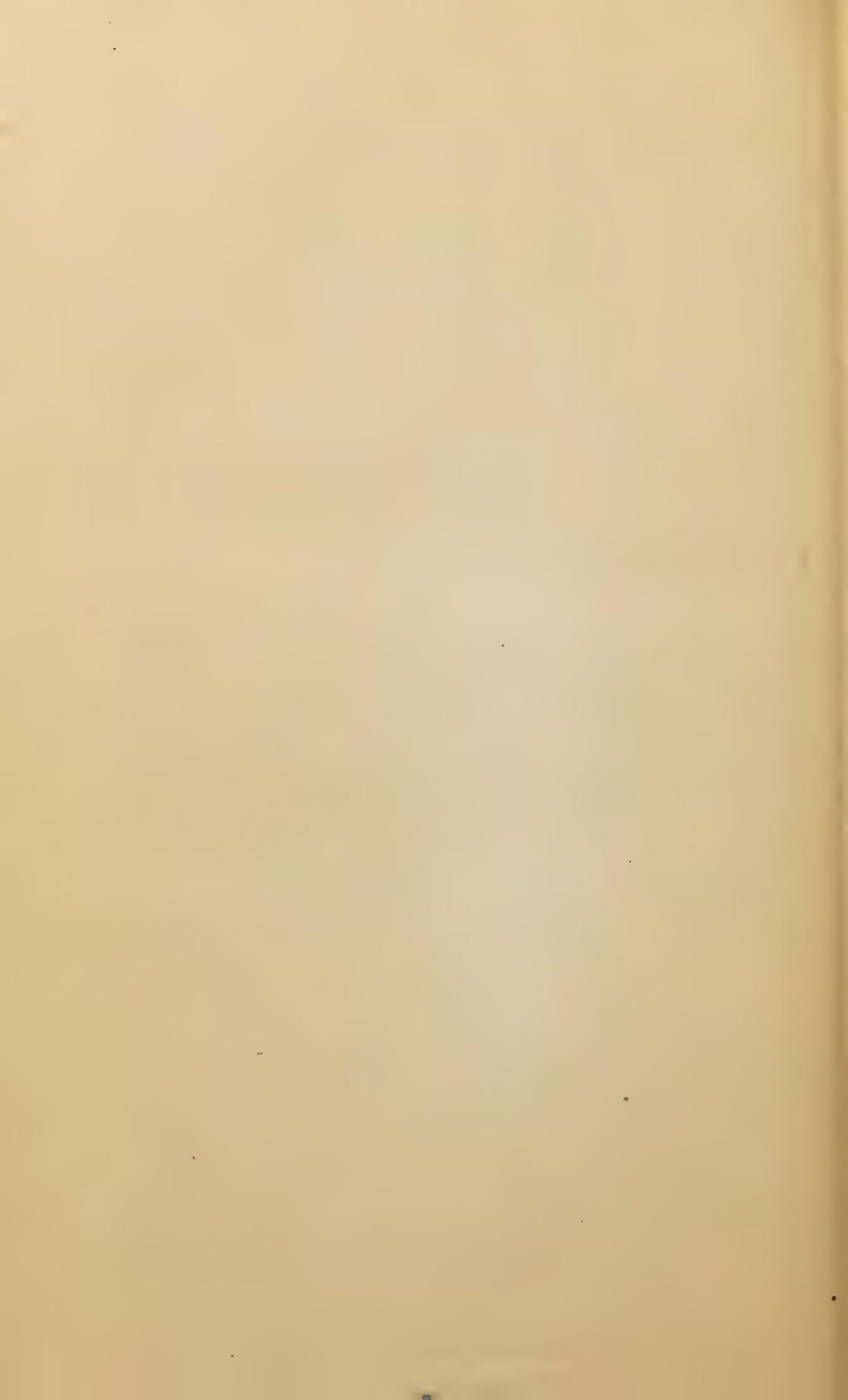
These men, however, generally occupy quite subservient positions and the number who become directors or reach positions where they exert real influence on the policy and development of the enterprise are few and far between."

*Pages 11-12.*—" . . . the pioneer work of the Technology Department of the City and Guilds Institute has exerted a great influence in the establishment throughout the country of technical education for the artisan in a wide range of crafts " by evening classes.

*Page 13.*—" All students, however, should be given the opportunity, but not be compelled, to broaden their outlook by contact with industry before or during the university course."

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## REVIEW OF THE WORK OF THE JOINT RESEARCH COMMITTEES, 1924-1943

OF THE IRON AND STEEL INSTITUTE AND THE BRITISH  
IRON AND STEEL FEDERATION REPORTING TO THE  
IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL

THIS review, published as Special Report No. 29, gives particulars of the origin, constitution, researches and publications to date of the four Joint Research Committees of The Iron and Steel Institute and The British Iron and Steel Federation. The following is a list of the main Committees and their Sub-Committees covered by the review :

The Committee on the Heterogeneity of Steel Ingots.

Ingot Moulds Sub-Committee.

Stresses in Moulds Panel of the Ingot Moulds Sub-Committee.

Joint Sub-Committee on the Physical Chemistry of Steel-making, a Sub-Committee appointed jointly by the Ingot Committee and the Open-Hearth Committee of the Iron and Steel Industrial Research Council.

Liquid Steel Temperature Sub-Committee.

Oxygen Sub-Committee.

Chemists' Panel of the Oxygen Sub-Committee.

Inclusions Sub-Committee.

Standard Methods of Analysis Sub-Committee.

The Alloy Steels Research Committee.

Thermal Treatment Sub-Committee.

Hair-Line Crack Sub-Committee.

Special Aero-Components Sub-Committee.

The Steel Castings Research Committee.

Moulding Materials Sub-Committee.

Foundry Practice Sub-Committee.

Foundry Steel Temperature Sub-Committee.

The Corrosion Committee.

Laboratory Research Sub-Committee.

Protective Coatings Sub-Committee.

Marine Corrosion Sub-Committee.

Sub-Committee on Low-Alloy Steels.

Sub-Committee on the Corrosion of Buried Metals, working in collaboration with the Committee on Soil Corrosion of Metals and Cement Products of The Institution of Civil Engineers.

Since the review was compiled (30th September, 1943) developments in the work of the Committees and Sub-Committees have necessitated several changes in their structure; at the time of writing (September, 1944) they are as follows:

The Oxygen Sub-Committee of the Ingot Committee, having completed its work on methods of determining gases in steel, has taken up researches in a wider field, and has been reconstituted as the Sub-Committee on Gaseous and Non-Metallic Inclusions.

To the Sub-Committees of the Steel Castings Research Committee have been added the Side-Blown Converter Practice Sub-Committee, with its Refractories Panel (reporting through the Sub-Committee to the Open-Hearth Refractories Joint Panel of the British Refractories Research Association and the Iron and Steel Industrial Research Council), and the Metallurgical (Steel Castings) Sub-Committee.

The Sub-Committees of the Corrosion Committee have been reorganised. The Laboratory Research Sub-Committee and the Sub-Committee on Low-Alloy Steels have been disbanded, a new Atmospheric Corrosion Sub-Committee and a Joint Planning Panel of the Protective Coatings and Marine Corrosion Sub-Committees have been set up, an Industrial Waters (Corrosion) Sub-Committee will be formed, and the Soil Corrosion Sub-Committee has been given this, a new, title.

All publications issued by these Committees and Sub-Committees have been published by The Iron and Steel Institute and will be found either in the *Journal* or in the Special Report Series.

## SECTION II.

# *A SURVEY OF LITERATURE ON THE MANUFACTURE AND PROPERTIES OF IRON AND STEEL, AND KINDRED SUBJECTS.*

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Abstractors and translators : Mr. R. A. RONNEBECK and  
Dr. D. R. STEINER.



## ORES—MINING AND TREATMENT

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**Manganiferous Waste from Concentration Plants and Attempts to Recover Higher Manganese Products from It.** G. G. Bring. (*Jernkontorets Annaler*, 1943, vol. 127, No. 5, pp. 129–149). (In Swedish). The manganese in Swedish ores is generally contained in the carbonate and silicate minerals associated with the ore, and only in exceptional cases is there any in the magnetite. The author describes attempts to recover a usable manganese-bearing product from these minerals. The methods tried were : (a) Wet-mechanical treatment on a vibrating screen ; (b) separation by strong or weak magnetic separators either with or without prior heat treatment ; (c) magnetic separation with A.C. separators ; and (d) flotation. On the whole the trials were unsuccessful, but the best results were obtained by heating to 900° C. followed by magnetic separation.

**Investigations of Slime Sedimentation.** S. Mortsell and T. Jensemfelt. (*Jernkontorets Annaler*, 1943, vol. 127, No. 6, pp. 169–224; No. 7, pp. 225–244). (In Swedish). The authors report on further investigations of the factors affecting slime sedimentation (see *Journ. I. and S.I.*, 1941, No. I., p. 118 a). The apparatus and experimental technique are described in detail. Rates of precipitation and the slime content of the clarified liquid were determined ; the former was recalculated to a “sedimentation index,” which is the time in seconds required for the main slime boundary to fall 1 cm. The materials investigated consisted of siliceous ore waste from the Rönnskär concentration plant and waste slimes from the concentration plants at Bålsjö, Sikfors and Persberg. By plotting the position of the main slime boundary in the sedimentation curve as a function of time, it was found that the rate of sinking of slime concentrations lower than the critical concentration remains constant within rather narrow limits. The rate of sedimentation at concentrations greater than the critical concentration is almost certainly proportional, not to the total height of the slime column, but to the height of the slime column above the point to which the slime is packed at the completion of sedimentation. The clarified liquid, *i.e.*, the layer of liquid above the main slime boundary, undergoes subsequent clarification with time, and the slime content of this liquid is approximately inversely proportional to the period of subsequent clarification. The sedimentation index increases relatively slowly with the concentration at low concentrations, but more rapidly at high concentrations. At low concentrations the clarified liquid becomes purer with increasing concentration, but at high concentrations the opposite relationship prevails. In the case of a slime of 100 g. per litre concentration and a sedimentation index of 50, this index increases by about 0·3 for every increase of

1% in the grain size of the slime with sizes below 0·060 mm. Changes in the grain size of slimes above 0·060 mm. appear to have little or no influence on the nature of the clarified liquid. The rate of sedimentation increases with the square of the temperature. No laws governing the influence of the pH value could be established, but pH values of 4·5-5·5 and about 9 appeared to be favourable for the sedimentation index and for the nature of the clarified liquid. The slime itself can dissolve in water, and the electrolytes thus formed have a marked effect on the sedimentation. For a basic sludge a basic precipitant, such as lime, should be most suitable, whereas an acid precipitant, *e.g.*, sulphuric acid, should give the best results with an acid slime.

**The Mechanical and Chemical Nature of Iron Ore Slig [Fine Ore Concentrate] from the Beneficiation Point of View.** H. Löwenhielm. (*Jernkontorets Annaler*, 1943, vol. 127, No. 8, pp. 333-366). (In Swedish). One method of utilising low-grade iron ores in Sweden is to crush them, fine-grind the crushed ore in a ball mill, subject the fines to wet magnetic separation and then briquette or sinter the product. This product of the wet magnetic separation, before sintering, is called "*slig*." The author discusses how changes in the grading of the fine ore concentrate affect the quality of the sinter made from it, and how the grading, from the sintering point of view, can be improved by a combination of magnetic separation and vibrating-screen treatment at less cost than by altering the grinding technique. Analyses of costs are presented which demonstrate the economic advantages of combining wet-magnetic separation with vibrating screen separation. Several designs of ball mill and vibrating screen are described and illustrated.

## FUEL

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**Modern Turbine—Types and Design.** F. K. Fischer. (*Iron and Steel Engineer*, 1943, vol. 20, July, pp. 49-58). The author reviews developments in the design of turbines supplied to iron and steel works in the United States. Of 104 turbines supplied in 1941, 19 were 25,000 kW., 13 were 35,000 kW., and 12 were 50,000 kW. Over 45% of them are operated at 850 lb. per sq. in.; about 55% at a steam temperature of 900° F.; as to speed, 77% run at 3600 r.p.m. and only 14·4% at 1800 r.p.m.

**Modulator Control for Multi-Fuel Fired Furnaces.** C. J. Geiser. (*Iron and Steel Engineer*, 1943, vol. 20, Aug., pp. 35-39). The author describes a modulator consisting of an inclined mercury U-tube working on a force-balancing principle, and its application to indicate the total of two or more fuel flows. It can also be used in conjunction with automatic proportioning devices and flow regulators.

**The Problem of Heating with Waste Gas at Swedish Ironworks.**

L. Malm. (*Jernkontorets Annaler*, 1943, vol. 127, No. 8, pp. 389-444). (In Swedish). The author reviews statistics relating to the utilisation of waste heat at Swedish iron and steel works and estimates that the total heat in the flue gases from blast-furnaces, steel furnaces and reheating furnaces is equivalent to a coal consumption of about 278,000 tons per annum, of which only a small proportion is at present utilised by recuperators, waste-heat boilers, &c. Calculations on waste-heat economy are presented and two particular cases are considered in detail. The first is a works comprising two blast-furnaces, one open-hearth furnace and four forging furnaces, and the second is one with three blast-furnaces, five open-hearth furnaces and a number of reheating furnaces for roughing mills, wire mills, plate mills and drop forges. In many cases a combination of waste-heat boiler plant and the preheating of air for reheating furnaces provides the best solution to the problem of waste-heat utilisation. The increased use of preheated air offers great scope for improvement under Swedish conditions.

**Occurrence of Phosphorus in Washington Coal and Its Removal.**

M. R. Geer, F. T. Davis and H. F. Yancey. (American Institute of Mining and Metallurgical Engineers, 1943, Technical Publication No. 1586). The authors report on trials to ascertain to what extent the phosphorus in Washington coking coals could be removed by washing. In the two beds studied the washing procedure for reducing the ash also satisfactorily reduced the phosphorus. In the other five studies the phosphorus was associated with clean coal rather than with the impurities and it could not be removed by ordinary methods.

**Pulverised Fuel for Metallurgical Furnaces.** C. S. Darling. (*Mechanical World*, 1943, vol. 114, July 16, pp. 60-63; July 23, pp. 102-104). The author quotes and discusses statistics relating to the consumption of pulverised coal and its economic advantages for heating air furnaces for pig-iron and malleable iron, billet reheating furnaces, and forging and heat-treatment furnaces.

**The Principal Function of Pulverized-Coal Burners.** H. Kreisinger and V. Z. Caracristi. (*Mechanical Engineering*, 1942, vol. 64, May, pp. 365-368). The authors discuss methods of obtaining an even distribution of fuel and air in furnaces fired with pulverised coal. Furnaces with burners directed downwards, horizontally and tangentially are considered.

**Briquetting Sub-bituminous Coal.** V. F. Parry and J. B. Goodman. (United States Bureau of Mines, June, 1943, Report of Investigations No. 3707). The authors report on laboratory investigations of the briquetting of American lignite and sub-bituminous coal. In particular, the briquetting properties of coal containing 25% of moisture, steam-dried coal containing 6% of moisture, and of air-dried coal containing 10% of moisture were studied. Raw or steam-dried sub-bituminous coal does not make briquettes equal in quality to briquettes of higher rank coal, no

matter how much binder is added to make up for the lack of caking properties of the coal.

**The B.S. Crucible Swelling Test.** R. A. Mott. (*Coke and Smokeless-Fuel Age*, 1943, vol. 5, Sept., pp. 165-170). The author describes foreign and British tests for coking coals and some applications of the British Standard Crucible Swelling Test. It seems to be true that coals with a swelling number of 9 should not be carbonised, unblended, in coke-ovens at a very fast rate of heating because the physical quality of the coke would suffer. At the other end of the scale there are coals which have insufficient swelling power for them to yield, when coked alone as smalls, a coherent coke of commercial quality. Below this there is the possibility that a coal will give a non-coherent powder. Generally speaking, a British Standard swelling number of over  $4\frac{1}{2}$  is desirable for a coal to be used alone for making metallurgical coke. Coals with lower swelling numbers can be used, if blended with more strongly swelling coals, for making metallurgical coke.

**Underfiring with Natural Gas-Air Mixture at Chicago.** G. A. Scott. (*Blast Furnace and Coke Association of the Chicago District*: *Blast Furnace and Steel Plant*, 1943, vol. 31, Aug., pp. 898-901). The author describes the fuel-gas metering, mixing and control arrangements at two batteries of Koppers cross-regenerative underfired coke-ovens at Chicago at which natural gas mixed with air is used for the fuel. The oven chambers are 37 ft. 6 in. long and 12 ft. high with an average width of 16 in.

**Increasing the Percentage Production of Large-Size Coke at Fast Coking Rates.** I. M. Roberts. (*American Institute of Mining and Metallurgical Engineers*, 1943, Technical Publication No. 1612). The author reports on tests with various additions to the customary coking-coal blends to find a means of increasing the proportion of large foundry coke in the total coke production. The additions tested included fly-ash from boilers burning coke breeze, coal dust high in fusain, petroleum-coke breeze, semi-anthracite and anthracite. Additions of 4-5% of anthracite fines caused a substantial increase in the average size of the coke produced in 19-20 hr. coking time.

**Increased Pig Iron Output through Improved Coke.** L. D. Schmidt, W. C. Schroeder and A. C. Fieldner. (*Eastern States Blast Furnace and Coke Oven Association*: *Blast Furnace and Steel Plant*, 1943, vol. 31, Aug., pp. 883-887, 902). The United States Bureau of Mines is surveying the coke industry to study methods of producing coke of higher quality and greater uniformity; the present paper is the first progress report of this survey. A list of problems and numerous suggestions for dealing with them are presented. When no preparation plants are available, the uniformity of coal can be improved by appropriate handling and storage at coke plants. Among the measures adopted are the following: (1) Stocking the coal in layers and making cuts down through

the various layers when taking it up for charging so as to obtain an average mixture of the coarse coal at the bottom and the fines at the top; (2) recording the storage time of the coal and using the longest stored first; and (3) reducing the danger of spontaneous heating and of deterioration of the coking properties by preventing or reducing the circulation of air through the stock pile.

**The Position of Low-Temperature Carbonisation.** (Coke and Smokeless-Fuel Age, 1943, vol. 5, July, pp. 135, 136, 138). The economic aspects and future possibilities of the low-temperature carbonisation industry in Great Britain are discussed. If a by-product market of sufficient value can be discovered, the very high price now demanded for low-temperature coke would be materially reduced. It is urged that the separate interests concerned with distilling tar, making gas and producing coke should take a wider view and should consider themselves as branches of the chemical industry.

**The Effect of Paraffins on the Nitration of Toluene.** W. L. Glowacki. (Eastern States Blast Furnace and Coke Association: Blast Furnace and Steel Plant, 1943, vol. 31, June, pp. 659-664; July, pp. 771-775). The author discusses the difficulties caused by the presence of paraffins in trinitrotoluene in a coke-oven by-product plant as this reduces the freezing point below the limit given in United States Government specifications, the methods of analysing toluene for paraffins and the steps taken to remove them.

## PRODUCTION OF IRON

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### **Increased Blast Furnace Capacity and How Accomplished.**

G. T. Williams and B. M. Stubblefield. (American Iron and Steel Institute: Blast Furnace and Steel Plant, 1943, vol. 31, June, pp. 645-648; July, pp. 780-782). The authors review the methods adopted in the United States to increase the production of pig-iron. Statistics on the erection of new furnaces and on relining and enlarging old ones are given. The times taken for relining and rebuilding have been considerably reduced by the simultaneous installation of the lining from the hearth to the mantle and from the mantle to the top, by the draining off of the furnace bear, and by precutting the hearth-blocks outside the furnace. Using sinter in the charge has increased production, but at high rates of blowing the advantages of sinter are not so great as at lower rates. The advantages of using sinter begin with 10-20% in the charge and increase until the charge contains 35-45%, but above this proportion the advantages do not increase directly with increasing sinter. The installation of equipment for removing moisture from the blast and increasing blowing rates have also contributed to increase the production of iron, but data are not published.

**Use of Inwall Temperatures in Determining Improper Gas Flow.**

L. Tofft. (Eastern States Blast Furnace and Coke Association : Blast Furnace and Steel Plant, 1943, vol. 31, July, pp. 759-766). The author continues the study by H. W. Johnson of the distribution of gases in the blast-furnace (see Journ. I. and S.I., 1938, No. II., p. 201 A). Temperature readings from four thermocouples at the inwall surface of a blast-furnace on a plane 10 ft. below the stock line were used as indicators of the gas-flow distribution. The previous and new methods of correcting uneven gas-flow by adjustments in the burden and in the quantity, temperature and pressure of the blast are described. The instructions for the new procedure are : (1) After tapping, return the blast volume to normal ; (2) raise the blast temperature to the maximum ; (3) give the blast a temporary severe check after each lowering of the big bell ; (4) do not permit the furnace to blow through until the blast pressure has increased by at least 5 lb. per sq. in., and allow hanging to continue until the stock slips of its own accord ; (5) give a mild check to the blast ; (6) reduce the blast temperature to normal ; and (7) reduce the blast quantity moderately. Curves showing the correlation between the above factors in actual blast-furnace operation are presented and discussed.

**The Electrical Conductivity of Molten Blast-Furnace Slags.**

A. E. Martin and G. Derge. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1569 : Metals Technology, 1943, vol. 10, Aug.). The authors review the literature on the ionic dissociation of slags and describe laboratory measurements of the electrical conductivity of some blast-furnace slags, as well as electrolysis experiments which indicate the identity of the ions present. Molten blast-furnace slags have high electrical conductivity and a high positive temperature coefficient of conductivity which indicate high degrees of ionisation. At a given temperature, the electrical conductivity of the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is to some extent related to the viscosity, the former increasing and the latter decreasing with increasing basicity. This probably means that, in the more basic slags, either ionisation is higher or the ions are smaller, and therefore more mobile. Silicon migrates with the negatively charged groups during electrolysis, calcium with the positively charged groups. A theory of slag constitution based on the results of this research and modern knowledge of glasses assumes that, as the atomic ratio of oxygen to silicon in the slag increases, the number of small silicate ions of the type (SiO<sub>4</sub>)<sup>-4</sup> and (Si<sub>2</sub>O<sub>7</sub>)<sup>-6</sup> will increase, and that constituents such as CaO, FeO and ferrites will become stable in basic slags, because it is only under these conditions that unsaturated silicate complexes will not tend to attract all available oxygen ions.

**The Ferroalloying Metals.** W. H. Dennis. (Metal Treatment, 1943, vol. 10, Autumn Issue, pp. 165-172). The author gives brief descriptions of the source, extraction, preparation and application

in the steel industry of the following alloying elements and materials : tungsten, molybdenum, manganese, vanadium, chromium, titanium, ferro-vanadium and ferro-silicon.

**The Production of Sponge Iron at Söderfors by the Wiberg Process.**

E. Améen. (*Jernkontorets Annaler*, 1943, vol. 127, No. 8, pp. 277-315). (In Swedish). The author describes trials at Söderfors in the production of sponge iron and the successful development of a suitable furnace and plant to operate the Wiberg process. The large furnace for full-scale production was built in the period 1930-32 ; fairly regular production was achieved by 1937, and by 1941 all the problems of any importance could be considered as solved. In 1942, 19½ tons of sponge iron per day were produced with a reduction efficiency of 85% ; the sponge contained total iron 77% with 65% in the metallic state. The energy consumption for carburising was 805 kWh. per ton of iron, the charcoal consumption 10.8 hectolitres per ton, and that of electrodes 2.7 kg. per ton. Cost calculations for producing sponge iron and pig-iron are presented and compared. Considerable economic advantage is achieved by using the sponge iron instead of charcoal pig-iron for steel-making. The melting of sponge iron is discussed, and it is shown that it is a suitable raw material for making high-quality steel in the electric-arc furnace.

**Powder Metallurgy.** F. V. Lenel. (*Mechanical Engineering*, 1943, vol. 65, July, pp. 489-492 : *Automobile Engineer*, 1943, vol. 33, Oct., pp. 415-418). **The Mechanical Properties of the Products of Powder Metallurgy.** F. V. Lenel. (*Metallurgia*, 1943, vol. 28, Aug., pp. 189-192). The author discusses the physical properties of parts made of iron by powder metallurgy. A part pressed from one end will have a greater density near the end at which pressure is applied than over the remainder of its length. It is not feasible to set up specifications for tensile strength, ductility, &c., to be determined on specially briquetted test specimens. Some testing machines for finished parts of various shapes are described. Indentation hardness tests are convenient and useful, but the mechanism of an indentation test on porous material must be understood. The lower the density the further will the indenter sink into the material. Two pieces may show identical hardness readings, but may have very different properties. One piece low in combined carbon, but high in density, will be quite ductile and shock-resistant, whereas another, having a high combined carbon content but a low density, will be quite brittle and shock-sensitive.

**Powder Metallurgy.** O. W. Ellis. (*Canadian Chemists : Canadian Metals and Metallurgical Industries*, 1943, vol. 6, July, pp. 26-30). The author discusses some of the fundamentals of powder metallurgy. In the special case of clean, spherical, solid particles of practically equal size of a metal which recrystallises shortly after it has been plastically deformed, the density of a compact increases with pressure until the theoretical bulk density is

closely approached; this relationship is not valid in the case of particles of a hard, brittle metal, of different sizes and shapes, varying in density and enveloped in adsorbed gas, oxide or other foreign matter—here, tensile strength depends on the total contact area between the particles on a given plane and is not related to the bulk density of the compact. The heat treatment of compacts in the purest hydrogen is, more often than not, quite as effective in reducing troubles due to oxides and, in certain cases, sulphides, as the use of deoxidants. The experience of the Ontario Research Foundation, and of P. R. Kalischer with alloys of aluminium, nickel and iron prove that, during heat treatment, it is imperative to use a carefully purified atmosphere with a dew point at about  $-60^{\circ}\text{C}.$ , so as to prevent the formation of oxides as a result of the decomposition of water vapour.

**The Scientific and Technical Principles of Powder Metallurgy and Its Sphere of Application.** W. Dawihl. (Iron and Steel Institute, 1943, Translation Series, No. 151). This is an English translation of a paper which appeared in *Stahl und Eisen*, 1941, vol. 61, Oct. 2, pp. 909–919. (See *Journ. I. and S.I.*, 1942, No. I., p. 219 A).

## FOUNDRY PRACTICE

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**The Foundry Industry and Air Warfare. VI. The Mass Production of Aerial Bombs.** (Foundry Trade Journal, 1943, vol. 71, Oct. 7, pp. 101–106, 100; Oct. 14, pp. 119–124, 128). An illustrated description is given of the equipment and practice at a foundry casting 500-lb. bombs in green sand moulds, using a maximum of steel scrap and a minimum of ferro-silicon. The plant consists of cupolas producing 20 tons of iron per hr., 12½-ton rotary Lesci furnaces and a battery of 3½-ton side-blown converters, with sand-cleaners, driers and mixing mills, and eight core-making machines.

**Gray Iron Foundry Classifies and Prepares Scrap for Cupola Melting.** K. J. Hepting. (American Foundryman, 1943, vol. 5, July, pp. 9–10). The author describes how an American foundry set up its own scrap-breaking and sorting department to deal with the mixed consignments of scrap it is now obliged to purchase.

**The Use of Basic-Lined Ladles in the Desulphurisation of Cast Iron by Sodium Carbonate.** N. L. Evans. (Iron and Steel Institute, 1944, this Journal, Section I.). A large tonnage of cast iron is desulphurised by treatment with sodium carbonate, the process normally being carried out in ladles lined with firebrick, ganister or similar siliceous refractory. These linings are attacked by soda slag, thereby impairing the efficiency of the process by contamination of the slag with silica. To meet demands for an improved degree of desulphurisation in the treatment of high-grade cast iron, the use of basic-lined ladles has been investigated. Refractories used

include calcined dolomite ("Basic"), magnesia, and stabilised dolomite, all of which result in greater sulphur reduction than can be obtained in siliceous linings. The most satisfactory material used so far is "Basic," bonded with tar, which is immune from attack by soda slags and has a long life. By its use it has been possible to reduce the sulphur content of certain high-grade cast irons to 0·01% or less.

Most of the work described has been carried out on a laboratory scale in a high-frequency induction furnace, but it has been supplemented by full-scale trials.

Methods of lining ladles are described, and the technique of repairing and patching is discussed. Sufficient evidence is not yet available to determine definitely whether monolithic or brick linings are preferable, but it is felt that, on grounds of economy and long life, there is much to be said for the former. Unfired bricks made of stabilised dolomite may provide a compromise so far as cost is concerned, and they are certainly an interesting departure from normal practice.

#### **Effect of Graphite Particle Size in the Inoculation of Gray Cast Iron.**

H. R. Dahlberg. (American Foundrymen's Association: Foundry, 1943, vol. 71, Aug., pp. 125, 128, 130, 146). The author describes a series of tests in which 250-lb. lots of cupola-melted grey iron were refined in a rocking electric furnace and then poured into 35-lb. ladles. During pouring the iron was inoculated with 12 g. of Mexican graphite of different particle size for each ladle. Test bars were cast at 2650° F. With low-silicon iron the transverse strength decreased markedly with increasing particle size. At above 2% of silicon the graphitisation is probably due more to the silicon than to the small amount of graphite added. Inoculation with graphite causes the iron to solidify in the stable iron-carbon system rather than in the metastable iron/iron-carbide system.

**Duplexing Malleable Iron.** R. Williams. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, June, pp. 34–36). The author describes the practice for making malleable iron castings at McKinnon Industries, Ltd., in Ontario. The composition of the cupola charge is silvery pig-iron 12%, foundry returns 49% and steel 39%. From 75 to 200 lb. of steel per ton are added to the heat in the 4-ton Moore Electromelt furnace, and the metal, which is tapped at 2800–2875° F., runs about carbon 2·50–2·55%, silicon 1·50–1·55% and manganese 0·40%. The malleableising treatment, which takes 38 hr., is carried out in a tunnel furnace 71 ft. long. This furnace has seven zones, as follows : No. 1 is raised to 1580° F. in 4 hr., in No. 2 the charge is held at 1750° F. for 6 hr., in No. 3 at 1700° F. for 6 hr., in No. 4 at 1675° F. for 6 hr., in No. 5 at 1420° F. for 2 hr., in No. 6 at 1360° F. for 8 hr., and in No. 7 at 1320° F. for 6 hr.

**Some Aspects of the Production of Malleable Iron Castings.** J. Roxburgh. (Institute of British Foundrymen; Foundry Trade

Journal, 1943, vol. 70, Aug. 26, pp. 341-345. vol. 71, Sept. 2, pp. 9-14; Sept. 9, pp. 29-33). See Journ. I. and S.I., 1943, No. II., p. 108 A.

**A Study of the Processes Involved in the Malleablising of Unalloyed and Alloyed Cast Iron in Carbon-Monoxide/Carbon-Dioxide Mixtures.** W. Baukloh, F. Schulte and H. Friedrichs. (Iron and Steel Institute, 1943, Translation Series No. 158). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 341-354. (See Journ. I. and S.I., 1943, No. II., p. 118 A).

**American Steel Foundries Cast Armor for Tanks.** F. G. Steinhbach. (Foundry, 1943, vol. 71, July, pp. 79-82, 172-176). The author describes the new steel foundry at East Chicago, Indiana, financed by the Defense Plant Corporation and leased to American Steel Foundries. The plant occupies 30 acres of floor-space and is equipped with very modern appliances for producing large and medium sized castings for armaments.

**The Contribution of the Steel Founder to Marine Engineering.** S. F. Dorey. (Institute of British Foundrymen : Foundry Trade Journal, 1943, vol. 71, Sept. 2, pp. 3-6; Sept. 9, pp. 25-28, 33). The author reviews some examples of large marine steel castings, such as stern frames, rudders, marine engine crank webs and armature rotors, and discusses the policy of Lloyd's Register of Shipping with regard to testing.

**Core Blowing in a Semi-Production Foundry.** Z. J. Madacev. (American Foundrymen's Association : Foundry, 1943, vol. 71, June, pp. 136-138, 230-233; July, pp. 86-88, 185). The author makes recommendations for core-blowing practice at foundries producing on a semi-mass-production basis. The limits of moisture for sands for small blowers are 1.8% to 2.2%, and for large blowers 2.5% to 3.5%.

**Allocate Core Costs to Individual Castings.** A. E. Grover. (Foundry, 1943, vol. 71, June, pp. 130-132, 223-225). The author describes a system of core costing in a foundry, explaining how the costs of materials, labour and overhead charges are allocated to each size and shape of core produced.

**Dries Molds in Continuous Oven.** P. Dwyer. (Foundry, 1943, vol. 71, Feb., pp. 89-90, 160-162). The author describes the grey iron foundry of the Kaukauna Machine Corporation in Wisconsin, where machine tools are made, with special reference to the moulding practice. The moulds are dried on a conveyor passing through an oil-fired furnace with a tunnel 52 ft. long and 10 ft. wide. Part of the tunnel constitutes a cooling zone, so that, on leaving it, the temperature of the mould is not too high to prevent the cores being put in.

**Continuous Casting.** L. H. Day. (Metal Treatment, 1943, vol. 10, Autumn Issue, pp. 173-180). The author describes with diagrams the following continuous casting machines : (1) The

Junghans; (2) the Williams; (3) the Eldred; (4) the Poland-Lindner; (5) the Hazelett "A"; (6) the Hazelett "B"; and (7) the Merle. The first four employ a stationary mould through which the metal is poured, whilst in the other three the metal is poured into the trough formed by two water-cooled turning rolls.

**Ford Casts Cylinder Barrels Centrifugally.** (Foundry, 1943, vol. 71, Aug., pp. 99, 180). A brief description is given of the casting operations at the Ford plant at Dearborn where steel cylinders 10 in. long and 6. in. in dia. for aero-engines are cast centrifugally. Eight mould-spinning machines are mounted on a turntable which stops at predetermined positions for loading, mould-spraying, pouring and unloading. Only a little rough-machining of the cylinders in the as-cast condition is required. Using this method there is a saving of 35 lb. of steel melted per casting as compared with ordinary foundry practice.

**Steel Sheaves Are Cast Centrifugally.** A. Johnson. (Foundry, 1943, vol. 71, June, pp. 139-140, 234, 235). This paper has been published previously under the title "Centrifuging during Pouring" (see Journ. I. and S.I., 1943, No. II., p. 150 A).

**Pours Steel in Cores Spun Vertically.** A. T. Baumer. (Steel Founders' Society of America: Foundry, 1943, vol. 71, July, pp. 94-95, 177). This paper has appeared previously under the title "Centrifugal Casting in Vertical Machines" (see Journ. I. and S.I., 1943, No. II., p. 111 A).

**Centrifugal Casting.** G. F. Alexander. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 71, Oct. 7, pp. 109-110). The author describes a James centrifugal casting machine for making tubes from which piston rings and cylinder liners are cut, and the melting practice adopted to produce small quantities of iron with carbon below 3.5% at a high casting temperature.

**Roughness of Metallic Surfaces, with Special Reference to Castings.** H. O'Neill and R. T. Insley. (Metal Treatment, 1943, vol. 10, Autumn Issue, pp. 181-187). The authors discuss the relative importance of surface roughness on forgings and castings, review methods of measuring surface roughness and describe specifications for mould dressings adopted by the London, Midland and Scottish Railway Co. Bronze plates were cast with various degrees of roughness and ten sets of five standards were prepared by eye sorting. A Schmaltz instrument was used to determine the surface roughness, and instead of averaging the heights of the crests, their root mean square was obtained and expressed in micro-inches (*i.e.*, millionths of an inch). On this basis, sets of five plates were made up in cases with a glass window to form "Roughness Comparscopes." The L.M.S. specifications for foundry blacking and foundry plumbago are cited. Natural flake graphite is better than artificial graphite for dressings. In doubtful cases the quality of plumbago can be determined by one of the three following methods:

(1) Microscopical examination at 750 diameters; (2) an electrical resistivity test; and (3) X-ray diffraction testing.

## PRODUCTION OF STEEL

**Brazilian Iron and Steel Developments.** (Iron and Coal Trades Review, 1943, vol. 147, Sept. 3, p. 367). A brief account is given of the extensions to the iron and steel works and rolling mills which are being erected by the Companhia Siderurgica Belgo-Minera at its works at Sabara and Monlevade in Brazil, and of the new works of the government-financed Companhia Siderurgica Nacional at Volta Redonda. The latter will be the first plant in Brazil to use coke as blast-furnace fuel. The output of finished steel at Volta Redonda is expected to be 220,000 metric tons per annum.

**Using Molten Pig-Iron in the Open-Hearth Furnace.** H. Willners. (Jernkontorets Annaler, 1943, vol. 127, No. 5, pp. 150-168). (In Swedish). The author reports on the work of a committee appointed by Jernkontoret to study the possibilities under Swedish conditions of decreasing fuel consumption and increasing steel production by charging molten pig-iron in open-hearth furnaces. The practice is advantageous in respect of both these factors. It was also concluded that: (1) The ratio of molten metal to cold scrap should be as high as possible consistent with a good life of the furnace hearth; (2) the method of charging, especially the time at which the molten metal is put in, is very critical and points to the advantages of a mixer; and (3) the temperature of the molten metal should be as high as possible.

**Survey of Liquid Steel Temperatures in Basic Open-Hearth Furnaces.** D. Manterfield. (Iron and Steel Institute, 1944, this Journal, Section I.). Temperature surveys have already been made on acid open-hearth furnaces and electric furnaces by other investigators. The object of the present work was to continue these investigations by temperature explorations on the larger type of basic open-hearth furnaces.

In the first part of the paper details are given of the type of furnace and slag dealt with in the survey. Temperatures were taken by means of the Schofield-Grace quick-immersion pyrometer, using a portable type of potentiometer for measurement. Readings were taken at various positions in the vertical and horizontal plane, and the results are tabulated and discussed. A point in the centre of the bath at a depth of 9 in. in the steel is the standard position for measurement. The mean deviation from this figure at all the positions explored was 5.5° C. (9.9° F.). It is concluded that a single temperature measured at the standard position can be taken as representative of the bath as a whole. The uniformity of temperature in the bath is shown to be governed by its activity. The second part

of the paper concerns the temperature fluctuations during the progress of a heat. A series of typical time-temperature diagrams is given, with details of the furnace additions. These show only a very temporary depression of temperature due to such additions. At the beginning of the refining period an average superheat (over the melting point) of 40° C. (72° F.) prevails, rising to 70–100° C. (126–180° F.) at the going-on stage. The response of the metal to alteration in flame conditions is also discussed. Finally a number of slag and metal temperatures was taken, the metal at the standard depth and the slag at a depth of 2 in. The results indicate that during the reaction period the activity equalises the temperature of both the slag and the metal. In the final stages of refining a greater difference was found. The slag temperatures were higher than the metal by from 1° C. (2° F.) to 47° C. (84° F.), depending upon the condition of the bath and the prevailing steel temperature.

#### **Wartime Production of Constructional Steels in the Basic Electric Furnace.** H. W. McQuaid. (American Iron and Steel Institute : Blast Furnace and Steel Plant, 1943, vol. 31, June, pp. 641–648 ; July, pp. 776–779). **Trend in Basic Electric Steelmaking.** H. W. McQuaid. (Steel, 1943, vol. 113, July 12, pp. 112–114, 142–148).

The author discusses steelmaking practice with the basic electric furnace. In charging, a small amount of light scrap is desirable on the bottom of the furnace inside the electrode circle with some of the heaviest scrap directly under the electrodes. Top-charging is generally best in furnaces of up to 40 tons, and the use of the charging machine is preferred for larger furnaces. The lime charged varies from one plant to another, the amount ranging from 2% to 4% ; some melters claim that 2% is adequate to retain the phosphorus in the slag as calcium phosphate, and that any further addition unnecessarily increases the resistance to the arc. At the end of the oxidation period the steel should be rapidly increasing in temperature (at least 2900° F.) ; the carbon should be about 10 points below the desired minimum, the silicon close to zero, and the residual manganese at about 0.20%. The removal of the first slag indicates that it is time to complete the deoxidation ; the temperature at this point is very important, and should be above 2900° F. to ensure sufficient fluidity. Full power is applied to the bath after making the alloy additions to overcome their chilling effect. The second slag of premixed lime, fluorspar and coke is then added, the amount usually being about 2% of the charge weight ; this slag is kept low in oxide by frequent surface additions of coke breeze. The timing of the addition of ferro-silicon is extremely important, for if the bath is not completely deoxidised there will be a tendency to excessive silicate inclusions ; this addition should not be made until equilibrium has been obtained between the bath and the slag. As soon as equilibrium can be reached with a slag containing less than 0.75% of iron oxide and more than 65% of lime, the melt is ready for tapping.

**Amplidynes for Arc-Furnace Control.** G. E. Shaad. (Blast Furnace and Steel Plant, 1943, vol. 31, Aug., pp. 879-882). The author explains how amplidyne generators can be applied to the control of the electrode movement in electric steel furnaces. Each electrode motor is driven by an individual amplidyne, the speed and rotation of the electrode motor depending on the voltage applied. For automatic operation, the control field of the amplidyne is supplied by a balanced control system in which a voltage proportional to the electrode current is opposed by a voltage proportional to the arc voltage. When these voltages are balanced, no field is applied to the amplidyne and zero voltage is applied to the electrode motor. As soon as a change in the furnace conditions upsets this balance, the two voltage vectors are no longer equal and the resultant voltage is applied to the control field. The resulting power output of the amplidyne drives the electrode motors, raising or lowering the electrodes until the voltage and current vectors are again in balance. The response of this method of control to changes in furnace conditions is practically instantaneous.

**The Behaviour of Fluorspar and of Calcium Phosphates in Relation to the Ferrous Oxide in the Melt and Its Metallurgical Significance.** W. Oelsen and H. Maetz. (Iron and Steel Institute, 1943, Translation Series No. 156). This is an English translation of a paper which appeared in Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung, 1941, vol. 23, No. 12, pp. 195-245. (See Journ. I. and S.I., 1942, No. I., p. 179 A).

## FORGING, STAMPING AND DRAWING

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**How Army Ordnance Forges 105-mm. High-Explosive Shell at Gadsden Ordnance Plant.** A. F. Macconochie. (Steel, 1943, vol. 113, July 26, pp. 72-78). The author describes and illustrates the machines and processes for the mass production of 105-mm. dia. shells from  $4 \times 4 \times 9$  in. billets at the ordnance plant at Gadsden, Alabama.

**Increase of Performance of Hot Work Tools.** W. Hauffer. (TZ für praktische Metallbearbeitung : Iron Age, 1943, vol. 152, Sept. 2, pp. 44-48). The author discusses factors affecting the performance of hot-working tools, such as forging dies, punches and mandrels. The surface of such tools is subjected to continual reversals of temperature, and these set up fatigue stresses; if the tool is water-cooled this may be aggravated by corrosion. The excellent performance of 14%-chromium steel for water-cooled punches is probably due to its high corrosion resistance. The resistance to tempering of a die steel containing 10% of tungsten used for making hot-pressed nuts was improved, and its performance increased by 20%, by increasing the hardening temperature from

2010° to 2150° F., but a further increase to 2190° F. tended to coarsen the structure and the tool life decreased again.

**Sheet Metal Work at the Puget Sound Navy Yard.** F. J. Oliver. (Iron Age, 1943, vol. 152, Aug. 19, pp. 45-49, Aug. 26, pp. 48-52). The author describes and illustrates some of the numerous forging presses, drop hammers, multiple punching machines and seam welding machines used at one of the United States Navy yards for making locker panels and doors, tool boxes, ventilating ducts, &c.

**Hot Cupping Used by Buick for 75-mm. Steel Cartridge Cases.** (Machinist, 1943, vol. 87, Sept. 11, pp. 121-128). A detailed account is given of the production methods set up by the Buick Division of the General Motors Corporation for drawing steel cartridge cases.

**Steel Cartridge Cases from Extruded Cups.** R. B. Schenck. (Metal Progress, 1943, vol. 43, June, pp. 912-916). The author describes the development work and the high-speed production method adopted by the General Motors Corporation for drawing 75-mm. steel cartridge cases.

**The Production of High Explosive Shell.** H. M. Lees. (Journal of the Junior Institution of Engineers, 1943, vol. 53, Sept., pp. 302-315). The author describes in detail the sequence of processes in the manufacture of 75-mm. shell from  $3\frac{1}{4} \times 3\frac{1}{4}$  in. billets, with special reference to the rough- and finish-machining operations.

**Carbide Dies for Steel Shell Cases.** E. Glen. (Wire and Wire Products, 1943, vol. 18, June, pp. 342, 356-357). The author points out the importance of proper maintenance of the carbide dies now used for drawing steel cartridge cases. A shell case entering the die presents a relatively sharp edge at the point where it meets the die approach angle and, in time, a very small "ring" is formed at this point of contact. As soon as this forms the die must be repolished to remove it.

**Temperature and Energy Conditions when Drawing through Multiple Dies.** E. Lueg. (Iron and Steel Institute, 1943, Translation Series No. 150). This is an English translation of a paper which appeared in Stahl und Eisen, 1943, vol. 63, Feb. 11, pp. 113-114. (See Journ. I. and S.I., 1943, No. I., p. 204 A).

## ROLLING-MILL PRACTICE

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**The Application of Mercury Arc Reflectors [Rectifiers] in Steel Mills.** A. D. Howry. (Iron and Steel Engineer, 1943, vol. 20, Aug., pp. 64-69). With steelworks and rolling mills operating at full capacity the problem of dealing with increasing peak demands on the electricity supply is brought to the fore. The author explains the principles and practical application of the mercury-arc rectifier for the supply of direct current to rolling mills and compares its technical and

economic characteristics with the alternative of motor-generator sets.

**Roll More Tons.** **V. Beam Calibrations.** A. E. Lendl. (Iron and Steel, 1943, vol. 16, July, pp. 460-464; Sept., pp. 532-536). Continuation of a series of articles (*see Journ. I. and S.I.*, 1943, No. I., p. 131 A). The author presents examples of methods of calibrating rolls for rolling beams.

**Effects of Temperature on Blooming Mill Production of Hot-Topped Steel.** H. J. Forsyth. (American Iron and Steel Institute: Blast Furnace and Steel Plant, 1943, vol. 31, June, pp. 638-640; July, pp. 767-770). The author discusses: (1) The effects of changes in ingot temperature on rolling rates, efficiency of personnel, power consumption and surface quality; (2) the responsibilities of the blooming mill in controlling the surface quality of typical killed steels; and (3) the possibilities of improving the heat control under present conditions. Finishing temperatures taken in the rolling of billets from ingots showed that, with only 20° F. increase, important savings in the rolling time were effected. At one mill the rolling time was reduced by 16% by an increase from 2000° to 2160° F. in the finishing temperature.

**Gauge Control in Cold Rolling Strip Mill.** J. D. Campbell. (Iron and Steel Engineer, 1943, vol. 20, Aug., pp. 52-62). In the rolling of strip in high-speed tandem mills the coil is threaded into the mill at a speed up to 600 ft. per min. and the mill is accelerated to top speed which may be 4000 ft. per min.; as the rear end of the strip is approached the mill is decelerated. During acceleration and deceleration the finished strip thickness passes beyond the tolerance limits and such strip is called "off-gauge." The author discusses two methods of automatically controlling the speeds of the mill stands, so as to reduce the amount of off-gauge material to a minimum. The first method is by automatic control of the shunt field strength of each mill motor, which is called "tapered tension control by motor field adjustment." The second is by an independent control of motor armature voltage over a limited range by series booster generators, called "control by *IR* drop compensating boosters." Results of tests, using multi-element oscillographs during rolling operations, are discussed, and the economic aspects of the two methods are compared.

**Palm Oil Control for Cold Mills.** C. E. Duffy. (Iron and Steel Engineer, 1943, vol. 20, Aug., pp. 31-34). The author describes the palm oil mixing, pumping and supply system installed at the cold rolling mill of the Bethlehem Steel Co. It had been found possible to use a mixture of palm oil 50% and water 50% and a very great saving in the consumption of palm oil was thus obtained. There are three main groups of equipment, namely, the proportioning, recirculating and regulating groups.

**Counting Devices Find Wide Use in Steel Industry.** S. H. Fuller. (Steel, 1943, vol. 113, Aug. 16, pp. 106-108, 134, 135). The author

gives numerous examples of the use of counting and indicating devices in steelworks, particularly in the rolling mills where applications include indicators for the gap between rolls, the lengths of strip on reels, the speed of rolls, the distance travelled by cranes, &c.

## HEAT TREATMENT

**Heat Transfer in Batch Heat Treatment of Metallic Strip.** O. G. Pameley-Evans. (*Metallurgia*, 1943, vol. 28, Aug., pp. 177-179). The author develops equations and gives examples of their use for calculating the rates of heat transfer through metal strip in coils and in packs of cut lengths. The equations take into account the thickness of oil films between the strips and the thermal conductivity of scale in the case of steel.

**Hard Surfaces on Steel.** D. Taylor. (*Journal of the Junior Institution of Engineers*, 1943, vol. 53, Sept., pp. 295-301). The author reviews the following methods of obtaining hard surfaces on steel: Cyaniding, pack carburising, gas carburising, nitriding, flame-hardening and induction hardening.

**"Case Depth"—An Attempt at a Practical Definition.** F. E. Harris. (*Metal Progress*, 1943, vol. 44, Aug., pp. 265-272). From the data obtained in gas-carburising tests on eight different steels (S.A.E. 1020, 2515, 3115, 4320, 4620, 4820 and National Emergency steels 8620 and 8720) by determining the carbon content at increasing depths and after increasing carburising times, and relating these to the carbon diffusion constants, the author derives tables and curves for ascertaining the carburising conditions which will produce a desired case depth and carbon content.

**Progress in Heat Treatment of Alloy Cast Iron.** J. S. Vanick. (*American Foundrymen's Association : Foundry*, 1943, vol. 71, July, pp. 90-92, 178, 179; Aug., pp. 96-97, 176-179). Cast iron may be heat-treated with the object of removing stresses, altering the mechanical properties, producing a particular microstructure, removing gases, full annealing, graphitising, or malleablising. The author presents several tables and series of curves which indicate the changes produced in low-alloy iron castings by various forms of heat treatment, and reviews the literature on this subject.

**Supposed Graphite in Carburized NE and S.A.E. Steels.** J. Welchner and R. W. Roush. (*Metal Progress*, 1943, vol. 43, June, pp. 889-896). A foreign grain boundary material has been observed in carburised gears made of NE 9420 and NE 9400 steels. The authors report on tests to identify this material and to determine the mechanism of its formation. The condition was more marked in pack-carburised parts than in gas-carburised parts. The above steels are low-alloy chromium-nickel-molybdenum steels. A number of S.A.E. steels as well as Armco iron were also tested using

different carburising compounds and gases. Barium-energised compounds produced the grain-boundary condition more than either calcium-energised compounds or natural gas. The amount of the foreign material formed increased with the holding time in the carburising medium and was independent of the heating up and cooling procedure. Both microscopical and chemical methods indicated that the grain boundary material was a silica and alumina mixture formed during the carburising. A theory explaining the formation of such a compound in a reducing atmosphere is put forward.

**The Use of High Frequency Induction Heating in the Heat Treatment of Metals.** A. L. Simmons. (Australian Institute of Metals : Australasian Engineer, 1943, vol. 43, June 8, pp. 18-19, 37, 39-41, 42, 43, 45-47). The author makes a comprehensive survey of the theory and practice of the induction heat treatment of metals. The theory of the transformation of radiant energy into heat is explained and details of methods of producing currents of different frequencies are given.

**Annealing Welded Boilers.** E. Larsson. (Teknisk Tidskrift, 1943, vol. 73, Aug. 21, pp. M81-M83). (In Swedish). The author describes an electrically heated furnace for annealing welded boilers with shell plating over 30 mm. thick. The furnace is cylindrical with a base 4·8 m. in dia. and a height of 4·1 m. The elements in the base total 78 kW. and those in the walls are arranged in three independently controlled zones of 110, 99 and 83 kW. capacity respectively.

**Mill Hardening.** J. Winning. (Mechanical World, 1943, vol. 114, Sept. 3, pp. 259-262). The author reviews papers by R. Schäfer and W. Drechsler on trials in German rolling mills on the possibilities of hardening rolled steel direct from the heat of rolling. (Abstracts of the papers in question appeared in Journ. I. and S.I., 1942, No. II., p. 214 A and 1943, No. I., p. 56 A.)

**Wartime Tool Steels.** H. B. Chambers. (American Society for Metals : Canadian Metals and Metallurgical Industries, 1943, vol. 6, June, pp. 24-26, 33). The author discusses the heat treatment of tool steels. The hardening temperature of tool steels covers a range of 100° F.; small sections should be quenched near the lower limit and large sections near the upper limit. A good general rule is to use the lowest third of the range for tools up to 1 in., the middle third for sections between 1 and 2 in., and the top third for sections exceeding 2 in. High-speed steel should not be held at the hardening temperature longer than is necessary for the temperature to become practically uniform throughout the section. In tempering, the longer the holding time at a given temperature, the more stress-relieved will be the tool. A minimum basis for the holding time at the tempering temperature is 1 hr. per inch of thickness for carbon and low-alloy tool steels, and 2 hr. per inch for high-chromium, hot-working or high-speed steels.

**Heat Treatment Plant for Steel Tools.** (Engineer, 1943, vol. 176, Sept. 10, pp. 213-214). A brief description is given of a plant recently installed by the L.M.S. Railway Co. for the heat treatment of high-speed and alloy steel tools. The furnaces are arranged in a straight line. The initial preheat is carried out in a furnace with forced air circulation. The tool is then transferred to an electrically heated salt bath, and thence to a similar salt bath operated at the required hardening temperature between 1230° and 1300° C. Quenching is done in another salt bath. There are also a salt-bath carburising furnace and a controlled-atmosphere muffle furnace.

## WELDING AND CUTTING

### A Tentative System for Preserving Ductility in Weldments.

**Part I.—The Problem and the Proposed Solution.** **Part II-A.—The Experimental Basis of the System.** G. E. Doan and R. D. Stout. (Welding Journal, 1943, vol. 22, July, pp. 278-S-294-S). The authors report on the progress of studies of the fundamentals of arc welding sponsored by the Engineering Foundation and carried out at several research institutions. A method is proposed for predicting, without resort to a welding test, the precise welding conditions which will result in a selected ductility in the heat-affected zone of a weld in any steel of the low-alloy or high-carbon type of any plate thickness and joint design. Hundreds of welds were made under different combinations of welding conditions using steel from the same heat. The results of these tests are given in Part II-A. A bar of the same steel was then held at 2100° F. for 30 min. to give it the same grain size as that reached in the hardest zone of any of the welds; a Jominy end-quench test was performed on this bar. One hardness reading on the Jominy bar corresponds to a hardness reading in one of the many tests, and thus represents certain welding conditions. The ductility associated with each hardness can be ascertained from four bend specimens of the particular steel quenched at different rates to cover the entire hardness range of the Jominy bar. The four specimens are bent until cracking occurs, and the hardness of that specimen which has the ductility specified for the welded joint required becomes the maximum permissible hardness; the Jominy test position of equal hardness will then indicate the welding conditions which will produce the specified ductility in the heat-affected zone.

### A Tentative System for Preserving Ductility in Weldments.

**Part II-B.—Jominy and Slow Notch-Bend Data on Various Steels.** J. H. Frye, jun. (Welding Journal, 1943, vol. 22, July, pp. 294-S-299-S). The author presents the results of bend tests on twenty-two low-alloy steels, and relates these to the results of Jominy end-quench tests to provide a basis for predicting the welding conditions

required to produce a given ductility in a welded joint. (See preceding abstract).

**Ship Plate, Cracked Weldings and Internal Stresses.** (Metal Progress, 1943, vol. 43, June, pp. 919-926). A collection of reports is published relating to the delivery of a few steel plates for shipbuilding, the tensile strength of which was less than 5% below that specified, as well as to the causes of the welded ship Schenectady breaking in two. R. E. Zimmerman reports on subsequent tests on the fractured ship plates and the drawing up of tensile test specifications. A special sub-committee of the American Bureau of Shipping reports on the probable causes of the breaking of the s.s. Schenectady, and R. T. Kinkead discusses residual stresses in welded structures.

**Residual Stresses in Welded Structures.** E. Chapman. (Iron Age, 1943, vol. 152, July 29, pp. 46-50). The author points out that at present the effects of thermal stresses in large welded structures are unpredictable and outlines the research programme decided upon by the Welding Stress Committee, which is a sub-committee of the Welding Research Committee of the Engineering Foundation.

**Control of Residual Stresses Through Welding Sequence.** M. Q. Cellers. (Iron Age, 1943, vol. 152, Sept. 2, pp. 50-56). The author describes and discusses the welding technique for obviating distortion and residual stresses as much as possible. Special reference is made to welding in shipbuilding.

**Stress Relieving in Welded Construction.** H. Lawrence. (Steel, 1943, vol. 113, Aug. 16, pp. 94-96, 133). The author explains the procedures for annealing, normalising, stress-relieving and tempering. Most stress-relieving specifications for welds require heating at 300-350° F. per hr. until 1150° F. is reached; the part is then held at this temperature for 1 hr. per inch of thickness and cooled at the same rate to below 200° F. Longer holding times tend to reduce the tensile strength.

**Welding Metallurgy.** W. G. Theisinger. (Iron and Steel Engineer, 1943, vol. 20, July, pp. 66-73). The author presents and discusses data on the effects of preheating steel to be welded and of different welding speeds on the residual stresses and hardness of the welded joint and the heat-affected zone.

## CLEANING AND PICKLING OF METALS

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**Pickling Steel Cartridge Cases.** A. J. Lehman. (Steel, 1943, vol. 113, Aug. 23, pp. 98-100). The author describes a unit for the rapid pickling of steel cartridge cases after annealing. In this unit the cases are rolled in a revolving drum of acid-resisting steel containing sulphuric acid. The drum has a spiral flange welded

on its inner surface, the pitch of which is just greater than the length of the cartridge ; this carries the cartridge from one end to the other as the drum revolves.

#### The Cleaning of Hot Steel before and during Rolling and Forging.

G. Wallquist. (*Jernkontorets Annaler*, 1943, vol. 127, No. 3, pp. 61-89). (In Swedish). There are three methods of removing scale from steel before or during rolling and forging ; these are : by purely mechanical means, by steam jets, and by high-pressure water. The last is the latest and the most effective method. The author discusses the high-pressure water method, the design and dimensions of the equipment and describes some tests made at Swedish works to determine the significance of the process in hot-rolling. A water pressure between 70 and 100 kg. per sq. cm. is required and the water is directed through a rectangular nozzle inclined at an angle to the surface of the moving billet or bar. The water is supplied from centrifugal or reciprocating pumps ; a modern plant generally has one or more three-cylinder pumps in conjunction with a compressed-air accumulator. The degree of cleanliness achieved can be measured by the weight of scale remaining per square metre of surface, or by the percentage of the initial scale removed. When ingots of 0·10% carbon steel were rolled down to thin sheet, the high-pressure water treatment reduced the amount of scale from about 330 to about 80 g. per sq. m. The water-jet treatment is excellent for improving the surface in the rolling of stainless steel and hollow drill steel. In the rolling of wire, the degree of reduction is great, and this in itself causes good mechanical cleaning. The degree of mechanical cleaning when rolling strip is not very good, so that water-jet treatment should be of value in this case. The efficiency of a cold strip mill was considerably increased by high-pressure-water cleaning equipment, as this removed most of the small sharp oxide and slag inclusions which are responsible for many pits in such strip ; this applies particularly to cold-rolled stainless steel strip.

## COATING OF METALS

#### Hundreds of Tests Show Lundbye Process Can Produce 300% Increase in Tool Life.

G. W. Birdsall. (*Steel*, 1943, vol. 112, June 14, pp. 100-104, 134-138 ; June 28, pp. 84-88, 127-129). The author describes the Lundbye process of chromium plating for increasing the life of high-speed steel tools containing up to 0·6% of carbon. The tool edge is sharpened before plating, and no finishing is done after plating. The tool is etched in hydrochloric acid for 30 sec. and then cleaned electrolytically. For the plating process the anode is preferably lead. Each gallon (United States measurement) contains 33 oz. of chromium trioxide dissolved in water with

an addition of 0.33 oz. of concentrated sulphuric acid. The bath is operated at 140° F. with a potential of 3.5–5 V. and a current density of 1.5–3.5 amp. per sq. in. depending on the material and shape of the work. The increased tool life obtained is due to the non-brittleness of the coating and the excellent adhesion obtained by the heat treatment which follows the coating process. This consists of immersing the plated tool for 1 hr. in an oil-bath at 350° F. During this treatment any hydrogen present passes out of the coating.

**Rolls for Sheet Galvanizing.** W. G. Imhoff. (*Steel*, 1943, vol. 112, Jan. 25, pp. 72–78; Feb. 8, pp. 88–90, 112). The author describes the rolling mechanism in hot-dip galvanising baths, discussing the materials used for the various parts and how adjustments and repairs are made.

**Electrolytic Tinning Lines Help Solve Tin Shortage.** R. A. Geuder. (*Steel*, 1943, vol. 113, July 19, pp. 126–128). The author gives a brief description of a continuous electrolytic tinning plant for tinning coils of cold-rolled strip at the Irwin Works of the Carnegie-Illinois Steel Corporation.

**The Future of Tinplate.** (*Iron Age*, 1943, vol. 152, July 29, p. 55). Data on the service life of food cans made of electrolytic and of hot-dipped tinplate are presented. Under war-time conditions, bonderised and lacquered coatings on steel sheet, with no tin, have proved satisfactory for certain foods, but after the war the tinned container will again become popular; the thickness of the tin will, in general, be less than formerly.

**The Recovery of Tin from Tin Cans.** R. E. Oesper. (*Journal of Chemical Education*, 1943, vol. 20, Aug., p. 406). The author describes a laboratory method of recovering tin from tinplate. The coating is stripped from the underlying iron or steel by treating with a boiling solution of sodium sulphide in which sulphur is suspended. Soluble sulphostannate is formed. This is decomposed by acidification with hydrochloric acid, and stannic sulphide is precipitated. When the sulphide is heated in air, stannic oxide is formed. Finally, the oxide is reduced by fusing with potassium cyanide.

**Phosphatising Iron and Steel Prior to Organic Finishing.** E. E. Halls. (*Metal Treatment*, 1943, vol. 10, Autumn Issue, pp. 188–197, 204). The author discusses the increased use of the bonderising process, especially under war-time conditions, and presents several tables of the results of salt-spray and other corrosion tests on panels coated with various enamels and paints with and without pre-treatment by bonderising. Among the many advantages claimed for bonderising, the following are of interest: (1) It overcomes the trouble of enamel tending to flow away from sharp edges and, therefore, on thin sheet metal it ensures that the enamel finish completely covers the edges; (2) when there are overlapping areas, as with folded seams, there is no retention of dangerous chemicals

in the seam, as there may be in electroplating processes; (3) the oxide tarnish produced in resistance welding or in flame welding need not be removed prior to bonderising; (4) it is not essential to remove millscale and heat-treatment scale prior to bonderising; (5) special primers and undercoats can be eliminated from the finishing scheme, and one finishing medium alone applied; and (6) plant expenditure is small and maintenance negligible.

**Black Finishes on Steel.** A. C. West. (Canadian Metals and Metallurgical Industries, 1943, vol. 6, June, pp. 32-33). The author describes three methods of producing a black finish on steel. In the first, the steel, after cleaning and pickling, is immersed in a concentrated alkali bath at about 290° F., and a uniform finish consisting of  $\text{Fe}_3\text{O}_4$  is produced in 10 min. This coating will prevent rusting indoors. The second method is phosphatising, and the third consists of giving the steel a zinc coating by one of the recognised methods and then blackening the zinc by immersion in a proprietary solution. Blackening the zinc does not increase its corrosion resistance, but it provides an excellent surface for painting.

**The Electric-Arc Preparation for Metal Spraying.** W. E. Ballard. (Metallurgia, 1943, vol. 28, July, pp. 105-107). The roughening of metal surfaces by "stroking" with electrodes to prepare them for metal spraying has already been described by W. C. Reid (see Journ. I. and S.I., 1943, No. II., p. 29 A). In this paper two methods are described using sources of current which are available at many works. In the case of a D.C. motor generator, the electrode consists of a bundle of steel wires, 5-8.2 mm. in dia., bundled at one end and slightly apart at the welding end; the work is made the negative pole. With A.C. equipment, the electrode consists of a bundle of 25-45 1-mm. ni-chrome wires.

**Alloy-Sprayer . . . Coats New Work, "Regalvanizes" Old Material, Patches Weld-Burned Areas.** (Steel, 1943, vol. 113, July 19, pp. 116, 139). A brief description is given of a metal-spraying pistol used with a lead alloy called "Galv-Welded Metal," which can be sprayed at about 500° F. The equipment is mainly for regalvanising areas where the original coating has been destroyed by welding.

**The Spraying of Metals by the Gas Method.** S. Brennert. (Teknisk Tidskrift, 1943, vol. 73, Aug. 14, pp. B61-B71). (In Swedish). The author describes metal-spraying pistols and the preparation of the surface to be sprayed, and discusses the properties of coatings of different metals. Curves are presented showing how the porosity of coatings of zinc, iron, lead, Monel metal and copper decrease with increasing thickness. With zinc and aluminium coatings on iron and steel, the base metal is protected by a galvanic effect, and it is not essential for the coating to be completely impervious to moisture. Thicknesses of about 0.15 mm. for zinc and 0.20 mm. for aluminium are sufficient. With the noble metals, however, the coating must be impervious to moisture, for here it is the iron which goes into

solution, and the atomic hydrogen forms on the sprayed metal; the thickness of the coating must therefore be greater.

**Sprayed Metal Reduces Maintenance Costs.** B. Granowski. (Mechanical Engineers Association : Australasian Engineer, 1943, vol. 43, June 8, pp. 16-17, 48). The author describes the metal-spraying process and tests on the adhesion and the effect of subsequent heat treatment. The average bond strength of coatings of various metals on a 1-in. dia. steel rod was 700 lb. per sq. in. when tested in the manner described. When making steel coatings on shafts the surface is roughened with a V-pointed tool making 20-30 cuts per inch. The spraying pistol is mounted above the centre line ; the peripheral speed is about 20 ft. per minute, while the pistol traverses about 0.010 in. per revolution of the shaft. If air is used to blow the steel on to the work the particles become coated with oxide and the coating is not homogeneous. Blowing with nitrogen reduces the amount of oxide sufficiently for recrystallisation of the deposit to take place with a short annealing treatment. A bar of 0.30% carbon steel was sprayed with 0.09%-carbon steel ; after annealing for 1 hr. at 900° C. the amount of oxide was so small that diffusion of the carbon from the core into the coating took place and all traces of the junction between the two metals disappeared.

**Protective Painting of Submerged Steel.** (Engineering Journal : Engineering, 1943, vol. 156, Aug. 27, pp. 167-168). Details are given of the methods employed by the Gatineau Power Co., Ottawa, to combat the corrosion of turbine headgates and deeply submerged sluice-gates. The corrosion occurs in fresh water with a pH value of 6.9. On deeply submerged parts, large soft tubercles are formed, under each of which is a cone-shaped depression in the metal which may attain a depth of  $\frac{1}{8}$  in. in ten years. After tests with over a hundred kinds of coating, the best results were attained from (a) heavy red-lead paints ; (b) bituminous coatings about  $\frac{1}{16}$  in. thick ; and (c) synthetic paints of the bakelite and rubber-base type. The procedure adopted is to wash and scrape off the tubercles and slime. The gate is air dried and then placed in a wooden housing containing electric heaters which heat the surrounding air to a temperature about 10° F. higher than that of the outside air. After cleaning by shot-blasting the gate is placed under a bank of infra-red lamps, which raise its temperature to 110° F. A priming coat of red-lead in linseed oil is applied on the side away from the lamps. The gate is reversed and the other face similarly painted. The lamps are kept on while three coats of red-lead paint are applied to all surfaces. A drying time of 32 hr. is allowed for each of the first two coats and 48 hr. for the third coat. The fourth coat consists of a heavy asphalt-base roofing compound containing asbestos fibres. At the temperatures stated, a gallon of red-lead paint, weighing 30 lb., covers about 675 sq. ft. The covering capacity of the heavy bituminous coating is about 100 sq. ft. per gallon.

**A Critical Study of the Theory and Practice of the Application of Radiant Heat to Metal Finishing.** J. H. Nelson and H. Silman. (*Sheet Metal Industries*, 1943, vol. 17, June, pp. 1039-1048; July, pp. 1213-1216, 1223-1225, 1229; Aug., pp. 1393-1402, 1417; Sept., pp. 1579-1582). The authors discuss the fundamental principles involved in the application of radiant heat to metal finishing processes. The transfer of energy by conduction and convection depends on the area involved and the difference in temperature, whilst with radiation, the transference is proportional to the area and to the fourth power of the temperature difference. From this it is deduced that radiant heating can best be applied to articles having a relatively small heat-absorbing capacity for their area, and requiring very rapid heating to a temperature not greatly in excess of their surroundings. Articles needing slow heating, or heating to a temperature very much above their surroundings, are not suitable unless radiators capable of large outputs are available. For efficient heat transfer, the temperature difference between the source and the work must be as high as possible and the air temperature in a radiant heating oven should be at such a level as to ensure the minimum transfer of heat by means other than radiation. An account is given of the history of the industrial application of radiant heating.

## PROPERTIES AND TESTS

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**Review of the Work of the Joint Research Committees, 1924-1943, of The Iron and Steel Institute and The British Iron and Steel Federation.** (*Iron and Steel Institute*, 1943, Special Report No. 29). The Joint Research Committees of The Iron and Steel Institute and The British Iron and Steel Federation are a group of some twenty-three research committees, sub-committees and panels reporting to The Iron and Steel Industrial Research Council; their aim is to increase current knowledge, both practical and theoretical, on the properties of steel. There are four main committees, the Heterogeneity of Steel Ingots Committee, the Alloy Steels Research Committee, the Steel Castings Research Committee and the Corrosion Committee. Their past and present work is briefly described and their proposed researches are indicated in separate sections; lists of the reports and papers published by the committees and of their personnel are given in appendices to the sections.

**Strength and Other Mechanical Properties of Cast Iron.** J. W. Donaldson. (*Metal Treatment*, 1943, vol. 10, Autumn Issue, pp. 157-164). The author reviews British, American and German investigations of the last three years on the static, torsional, impact, fatigue and damping characteristics of high-duty and alloy cast irons.

**The Strength of Metals.** L. Bragg. (*Teknisk Tidskrift*, 1943, vol. 73, Aug. 14, pp. 403-407). (In Swedish). The author explains the structure of metals and the phenomena associated with slip, illustrating the principles involved with an apparatus in which one mass of minute soap bubbles is moved over another.

**The Effect of Speed of Loading upon the Ductility of Steel Structural Members.** W. M. Wilson. (*Welding Journal*, 1943, vol. 22, July, pp. 317-S-325-S). The author reports on the work of G. L. Jeppesen and R. Zaborowski who determined the effect of the speed of loading on the ductility of steel. Jeppesen determined the elongation of carbon and low-alloy structural steels when broken in tension by a falling weight, and Zaborowski performed similar tests using a heavier falling weight on riveted and welded joints, as well as plates of considerable width and thickness without joints. The reduction of area was at least as great with a 10-ft. drop as for the static test, or with a 2-ft. drop. The elongation was slightly greater with a 10-ft. drop than with a 2-ft. drop or the static test.

**Effect of Carbon on Alloy Steel Ductility.** M. F. Hawkes. (*Iron Age*, 1943, vol. 152, July 22, pp. 49-50). The author presents data on the changes in elongation and reduction of area with the carbon content of alloy steels tempered from the fully hardened state to tensile strengths of 150,000 lb. and 200,000 lb. per sq. in. The decrease in reduction of area with increasing carbon content is slightly greater than the decrease in elongation. In the latter, the decrease is very small between 0·12% and 0·80% of carbon.

**An Investigation of the Technical Cohesive Strength of Metals.** D. J. McAdam, jun., and R. W. Mebs. (*American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1615 : Metals Technology*, 1943, vol. 10, Aug.). The authors report on an investigation of the tensile properties of notched cylindrical specimens of oxygen-free copper, Monel metal, 13/2 chromium-nickel steel, a 0·2% carbon steel and a 0·04% carbon steel, from the results of which curves are derived showing the influence of notched dimensions and angle, and of previous plastic extension on the technical cohesion limit, ultimate stress, yield stress and ductility. The influence of combinations of axial and radial uniform stresses on the technical cohesion limit, yield stress and ultimate stress, and of plastic extension on the technical cohesive strength is discussed.

**Some Factors Affecting Longitudinal Bend Tests on Fine-Grained, Cold-Rolled Annealed Carbon Strip Steel.** A. F. Sprangle and M. A. Hughes. (*Transactions of the American Society for Metals*, 1943, vol. 31, June, pp. 257-280). The authors report on tests to determine the effect of the chemical composition, degree of cold reduction and annealing time on the cracking tendency of steel strip when bent flat upon itself in the direction of rolling. Steels with 0·15-0·20% of carbon were free from visible cracks in this test, irrespective of

the manganese content or the degree of reduction prior to annealing. The medium carbon steels (0·50–0·60%) required at least 35% reduction to give good bend-test results with minimum annealing times, and a low manganese content seemed to be desirable. High-carbon steels (0·85–0·95%) could not be bent flat, but showed different degrees of cracking when bent on a radius equal to twice the thickness; a minimum of 45% cold reduction prior to annealing was required to obtain satisfactory bend-test results.

**Brittle Coatings for Quantitative Strain Measurements.** A. V. de Forest, G. Ellis and F. B. Stern, jun. (Journal of Applied Mechanics, 1942, vol. 9, Dec., pp. A-184–A-188). The authors describe the technique for employing brittle lacquer coatings on strips of metal to make strain measurements. The most convenient form of test is to use a steel strip  $12 \times 1 \times \frac{1}{4}$  in. as a cantilever beam held at one end of a stand by an adjustment screw which lifts the other end of the strip against a cam designed to apply a known deflection load. This deflection is such that the upper surface of the coating (0·004 in. thick) on the strip will exhibit varying amounts of strain when pressure is applied by turning the cam. Strain patterns in the form of closely spaced lines across the strip appear in the coating when the load is applied. The strip is released from the stand and placed against the scale from which the amount of strain is read. The effects of changes in the coating thickness, drying time and temperature, and of bubbles in the coating, are explained. The practical application of the method is illustrated by correlating the strain patterns obtained on a sewing-machine head in a static test and the fatigue failure of the same part in service.

**Fatigue Strength of Machinery under Alternating Stresses.** R. A. Collacott. (Steam Engineer, 1943, vol. 12, Sept., pp. 345–347). The author discusses factors leading to the inception of fatigue failures, and stresses the importance of avoiding abrupt changes in section in design, and preparing steel surfaces free from pits and scratches.

**Effect of Screw Threads on Fatigue.** S. M. Arnold. (Mechanical Engineering, 1943, vol. 65, July, pp. 497–505). The author reviews the literature on the fatigue testing of threaded members and screwed joints. A bibliography of 167 references is appended.

**The Useful Data to be Derived from Fatigue Tests.** J. O. Almen. (Metal Progress, 1943, vol. 44, Aug., pp. 254–261). The author points out that laboratory fatigue-test data cannot readily be applied in the design of engine parts because such parts cannot be finished with the care and exactness that are given to laboratory specimens. In the practical testing of parts, comparisons of material, design or processing cannot be made unless the tests are run to failure. Thus, in presenting test results, study should not be directed so much to the endurance limit (where, for steel, life is infinite), but to that portion of the stress/number-of-cycles curve to the left of the "knee" where life is finite. In such fatigue curves for

engine parts the slope of this part of the curve is almost invariably steeper than that for laboratory test specimens of the same material. If sufficient test data are plotted, two scatter bands can be drawn, one for tests on parts and the other for laboratory test specimens, and these bands will intersect at a position indicating a stress approaching the ultimate tensile strength of the material. This stress and the corresponding number of cycles can be taken as a criterion of the true fatigue strength of the parts.

**The Bending Fatigue Strength of Machined Crankshafts after Straightening, with Notes on the Stress Distribution, Obtained by Extensometer and X-Ray Diffraction Measurements.** R. Schmidt. (Iron and Steel Institute, 1943, Translation Series, No. 157). This is an English translation of a paper which appeared in *Luftwissen*, 1942, vol. 9, Sept., pp. 263-267.

**Effect of Surface Treatment on Fatigue Strength.** H. Wiegand. (Iron and Steel Institute, 1943, Translation Series, No. 155). This is an English translation of an article entitled "Oberfläche und Dauerfestigkeit" published in 1940 by BMW Flugmotorenbau, Berlin.

**Selection of Toolsteel by Its Hardenability.** S. M. DePoy. (Metal Progress, 1943, vol. 43, June, pp. 917-918). The author reproduces cooling rate curves from the S.A.E. Handbook, 1942 edition, which show the changes in cooling rate from centre to outside of round bars up to 4 in. in dia., and explains how to use these in conjunction with Jominy end-quench hardenability curves to predict the type of toolsteel and the heat treatment required to produce given core and surface hardness.

**A New Microhardness Measuring Instrument.** R. Woxén. (Teknisk Tidskrift, 1943, vol. 73, Sept. 18, pp. M93-M98). (In Swedish). After discussing static methods of measuring hardness, the author describes and illustrates a new microhardness tester with which the difference in impressions between those obtained with an initial load of a few grammes and a final load of up to 1 kg. can be accurately measured. The Vickers hardness number can be calculated from the values obtained. The instrument can be used for metals of any hardness, for determinations on single crystals and for very thin surface layers.

**The Reduction in the Stress in Steel Bolts under Load at High Temperatures.** K. Wellinger and E. Keil. (Iron and Steel Institute, 1943, Translation Series, No. 154). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1942, vol. 15, Apr., pp. 475-478. (See Journ. I. and S.I., 1943, No. I., p. 211 A).

**Mechanical Properties of Iron-Phosphorus Alloys.** J. K. Stanley. (Iron Age, 1943, vol. 152, Aug. 19, pp. 42-44). The author reports the results of comparative tests on small ingots of electrolytic iron and of iron-phosphorus alloys containing 0·25%, 0·46%, 0·65% and 0·86% of phosphorus. The alloys with up to 0·46% of phos-

phorus were readily cold-rolled ; the 0·65%-phosphorus alloy could be rolled with care, whilst that containing 0·86% could not be cold-rolled. The tensile strength, yield strength and hardness increased linearly up to 0·46% of phosphorus ; with more phosphorus the change was only slight. The elongation was 30% or higher up to 0·46% of phosphorus but it decreased rapidly with higher concentrations.

**Production Experience with National Emergency Steels.** R. W. Roush. (S.A.E. Journal, 1943, vol. 51, Mar., pp. 84-93). The author describes the steps leading to the drawing up of the specifications of the National Emergency steels and discusses the properties of some of them, in particular those suitable for gears.

**Intensifying of NE 9422 Steel.** (Iron Age, 1943, vol. 152, Aug. 19, pp. 50-51). The results of tests are presented which show the effects of treating steel NE 9422 with Grainal on its properties in the oil-hardened and water-hardened state. Steel NE 9422 is a low-alloy chromium-nickel-molybdenum steel.

**User Report No. 15 on Experience with NE (National Emergency) Alloy Steels.** R. W. Emerson. (Steel, 1943, vol. 113, July 26, pp. 88-96). The author reports the results of hardness surveys and other weldability tests on NE steel 8339, which is a manganese-molybdenum steel used for making tubes.

**User Report No. 16 on Experience with NE (National Emergency) Alloy Steels.** A. Zwald. (Steel, 1943, vol. 113, Aug. 2, pp. 94-95, 130, 131). The author reports the results of tests on specimens of cast steel NE 9437, which is a low-alloy chromium-nickel-molybdenum steel. A set of crane gear wheels up to 9½ in. in dia. was made of this cast steel, as forgings could not be obtained quickly. The results of X-ray examination and mechanical tests were good and the cast gears have given good service.

**User Report No. 17 Presents Experience of an Aircraft Manufacturer with NE (National Emergency) Alloy Steels.** W. Kahn, jun. (Steel, 1943, vol. 113, Aug. 23, p. 107). The author gives brief particulars of the properties of some of the low-alloy NE steels which have been substituted without difficulty for S.A.E. steels in the construction of aircraft.

**Standardisation and Use of Alternative Steel Products in War-time.** T. Stevenson. (Iron and Coal Trades Review, 1943, vol. 147, Oct. 8, pp. 537-539). The author describes the steps taken by the Iron and Steel Control in collaboration with the Ministry of Supply and the British Standards Institution to reduce the consumption of steel in Great Britain.

**Malleable Iron Castings in Ordnance.** J. H. Frye. (Steel, 1943, vol. 113, Aug. 23, pp. 95-96, 126, 127). The author describes many new applications of malleable iron castings in army vehicles, tanks and gun mountings.

**Exhaust Valves for High-Duty Internal Combustion Engines.** C. A. E. Wilkins and W. J. Currie. (Metal Treatment, 1943, vol. 10,

Autumn Issue, pp. 147-152, 201). The authors discuss the effects of tetra-ethyl-lead fuels on exhaust valve materials, methods of combating the very corrosive attack of the exhaust condensate, and other difficulties connected with the life of internal-combustion engine valves. Exhaust valves attain temperatures of 700-900° C., and under these conditions Silchrome valves have a poor corrosion resistance, whilst austenitic high-nickel-chromium valves are completely resistant. The attack of the hot gases can be counteracted to some extent by welding a deposit of Stellite on the valve faces, but the success of this depends greatly on the skill of the welder. Various types of valve failure are reviewed. Burning appears to have its origin in small gas leaks or fine cracks; cracking either from inherent defects in the valve material, or from radial cracks formed in the scale of the valve seat; and broken valves from fatigue cracks apparently commencing from small corrosion pits. The valve stem should be as hard as possible and have a very good surface finish.

## METALLOGRAPHY AND CONSTITUTION

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**Expansion of Metallografiska Institute.** M. Tigerschiöld. (*Jernkontorets Annaler*, 1943, vol. 127, No. 7, pp. 245-258). (In Swedish). The author gives a brief account of negotiations which have taken place and culminated in an agreement between Jernkontoret (Swedish Ironmasters' Association), Mekanförbundet (Association of Swedish Engineering Works), Metallforskningsföreningen (Metal Industry's Investigation Association), and the Swedish State, to build and equip new laboratories in Stockholm for Metallografiska Institutet. The financial arrangements, constitution of the governing council and scope of the investigations to be undertaken are outlined.

**Interference Fringes for the Measurement of Surface Micro-Topography.** J. F. Kayser. (*Metal Treatment*, 1943, vol. 10, Autumn Issue, pp. 153-156, 172). The author describes a method of measuring the contour of reflecting surfaces, particularly glass and metallic surfaces.

Interference fringes are produced on the surface by passing the light from the vertical illuminator of a metallurgical microscope through a combination of Ilford Micro 3 and Micro 5 filters. The method is applicable to finely-finished flat or convex surfaces. It cannot be used if the average height of the surface above the mean line exceeds about  $20 \times 10^{-6}$  in. For flat and cylindrical surfaces magnifications below 25 or above 500 are seldom, if ever, required.

**Electron Diffraction.** (*Steel*, 1943, vol. 113, Aug. 23, pp. 92-93). A brief description is given of an electron diffraction camera developed by the Westinghouse Electric and Manufacturing Co.

for obtaining electron diffraction patterns of the surface of specimens which, while in the camera, are subjected to attack by a corrosive agent, or to the influence of heat.

**The Technique of X-Radiography and Notes on Gamma Ray Methods.** A. G. Peacock. (*Welding*, 1943, vol. 11, Oct., pp. 443-452). The author explains the principles of radiography and describes the technique of applying it to the examination of welds. Methods of controlling scatter, the use of filters and screens, geometrical considerations, processing films and the interpretation of radiographs are discussed. Finally, the technique of gamma radiography is described. Gamma-ray equipment has the advantage of great portability. No power supply is necessary, and welds can be examined in the field. Great penetrating power and freedom from scatter are also advantageous in certain cases. The serious disadvantage is the long exposure time.

**A Recording Microphotometer for the Examination of X-ray Diffraction Films.** H. R. Ronnebeck. (*Journal of Scientific Instruments*, 1943, vol. 20, Oct., pp. 154-161). After enumerating the technical difficulties to be overcome in designing a recording microphotometer for examining X-ray diffraction films, the author describes in detail the mechanical construction, optical system and the electrical circuits of a new design suitable for manufacture out of parts which were readily available. Alternative forms of photoelectric recording are discussed, the final choice being a photocell-photometer unit with an amplifier and Einthoven string galvanometer. Two old cinema "sound heads" were used for the optical scanning. The recording is done at a film speed of about 3·0 cm. per min. Some specimen recordings are reproduced and discussed. A bibliography with 95 references is appended.

**A Note on the Microstructure of High-Silicon Acid-Resisting Iron.** J. E. Hurst and R. V. Riley. (*Iron and Steel Institute*, 1944, this Journal, Section I.). An unusual type of etched structure, referred to as the "barley shell" structure, has been described by various investigators of the iron-silicon alloys. The authors have observed it in their examination of commercial iron-silicon alloys containing upwards of 10% of silicon, and have recorded some conditions of etching under which it is obtained and some observations on its characteristics. It is readily obtained by etching with a reagent containing picric and hydrofluoric acids. It is not a true or real structure of the alloys, but its formation under the observed conditions is a characteristic of high-silicon iron alloys.

**The Occurrence of the Carbide Phase in High-Silicon Iron-Carbon Alloys.** J. E. Hurst and R. V. Riley. (*Iron and Steel Institute*, 1944, this Journal, Section I.). The authors record the presence of a carbide constituent in commercial iron-carbon-silicon alloys containing 10-15% of silicon. This carbide is found to be present on rapid solidification of the alloy followed by a quick rate of cooling in the solid state. On annealing, the carbide constituent decom-

poses with the formation of "fine graphite" and presumably silicoferrite. The influence of alloying elements upon the stability of the carbide was investigated and found to be similar to the action of the same elements on the cementite in low-silicon iron-carbon alloys. The true identity of the carbide has not been established, but it is shown that it cannot be regarded as pure cementite.

**The Structure of Martensite.** H. Lipson and Audrey M. B. Parker. (Iron and Steel Institute, 1944, this Journal, Section I.). Some new experimental evidence concerning the structure of martensite has been obtained. It appears that the iron atoms do not lie in an exactly regular arrangement in the tetragonal lattice, such as at the corners and centres of the unit cells, but have a range of structural parameter along the four-fold axis. The mean value of this parameter for a 1·57% carbon steel is about 0·06, which gives a mean displacement, from the special lattice points mentioned above, of about 0·18 Å.

Spatial considerations show that this displacement is such that the octahedral interstices, which Petch (see Journ. I. and S. I., 1943, No. I., p. 221 A) considers to be the most likely positions for the carbon atoms, are enlarged sufficiently to accommodate a carbon atom. This removes the main objection, pointed out by Hägg, to this theory of the positions of the carbon atoms.

The experimental work was done on small rods so that the X-ray and microscopical examinations and the chemical analysis could all be carried out on the same specimen.

Evidence for the displacement of the iron atoms has been obtained from the values of the intensity ratios of the X-ray line doublets given by the tetragonal structure.

**The Iron-Nickel Phase Diagram by Magnetic Analysis and the Effects of Cold-Work.** K. Hoselitz. (Iron and Steel Institute, 1944, this Journal, Section I.). The method of using measurements of magnetic saturation intensity of quenched and annealed iron-nickel alloys for the determination of equilibrium phases is briefly described. Previous studies of the thermal hysteresis phenomena and processes of phase changes have enabled a more complete equilibrium diagram of the iron-nickel system to be obtained than had before been possible. The slow rate of approach to equilibrium in these alloys necessitated the exploration of methods to expedite phase-change processes. With this aim in view, the magnetic saturation intensities of iron-nickel alloys which had been subjected to cold-work were examined over a wide range of temperatures. The methods of analysis developed in earlier work were applied to these experiments.

Whilst the annealing of cold-worked alloys gives inconclusive results, the effect of cold-work on quenched alloys produces marked changes in certain of the alloys, particularly between 29% and 35% of nickel, where the original single-phase alloys actually show a distinct separation into two phases. This can be seen by comparing

their saturation-intensity/temperature relationships before and after cold-work. In alloys containing less nickel the changes are small, because these alloys are presumably not so far from their equilibrium state. In general, it can be concluded that cold-work alone brings about a certain amount of change towards equilibrium conditions, and in this case these experiments may prove of value in an attempt to determine the state and changes occurring in the alloys of nickel and iron at low temperatures.

**The Thermal Diagram of the System Iron-Tin.** W. F. Ehret and G. H. Gurinsky. (American Chemical Society: Iron and Steel, 1943, vol. 16, Sept., pp. 543-544). See Journ. I. and S.I., 1943, No. II., p. 202 A.

## CORROSION OF IRON AND STEEL

**Some Measurements of Corrosion-Fatigue Made with a New Feeding Arrangement.** A. U. Huddle and U. R. Evans. (Iron and Steel Institute, 1944, this Journal, Section I.). A new method of feeding corrosive liquid to a steel rod rotating in a fatigue-testing machine provides a sharply-defined ring of liquid renewed from a wick which neither touches nor appreciably shields the steel surface. This has been used to study the loss of strength and elongation which occur in a rod subjected to alternating stresses when wetted with sea water; the deterioration of mechanical properties does not become serious until half the corrosion-fatigue life has elapsed. Coating with a paint richly pigmented with zinc dust increases the life; this is, in general, partly due to electrochemical protection and partly to mechanical exclusion.

**Identification of Rust on Iron and Steel.** R. O. Clark. (Industrial and Engineering Chemistry, Analytical Edition, 1943, vol. 15, July 15, pp. 464-465). The author describes a simple method of identifying rust on lubricated ferrous alloys. Visual inspection could not be relied upon to distinguish between rust and petroleum gum. It was found that gelatin paper moistened with water was capable of removing sufficient rust for testing, without affecting the metal itself. The paper is prepared by fixing unexposed glossy photographic paper in sodium thiosulphate solution, treating in a hypo-eliminating solution and drying. After removal from the specimen, the paper is immersed in hydrochloric acid containing potassium ferrocyanide. On development a blue pattern of the rusted surface is obtained.

**Corrosion by Sea-Water : A Review of Recent British and American Investigations.** J. W. Donaldson. (Metallurgia, 1943, vol. 28, Aug., pp. 163-170).

**Unusual Corrosion Difficulties and Their Solution.** F. Alton. 1944-i

(Engineering and Boiler House Review, 1943, vol. 57, June, pp. 166-169; Aug., pp. 211-215). The author reviews some corrosion problems encountered at large German boiler installations, basing his information on a report by M. Werner on feed-pump corrosion and one by W. Wesly on the use of ammonia to prevent corrosion by oxygen-free condensate; these reports appeared in Korrosion und Metallschutz, 1942, vol. 18, pp. 158 and 164.

**Promotion of the Corrosion of Iron in Alkaline Solutions by Zinc and Aluminium.** G. Nilsson. (Nature, 1943, vol. 152, Aug. 14, pp. 189-190). The author describes some experiments which illustrate the difference between the behaviour of passive and active iron in the same alkaline solution. With passive iron the attack, if any, is very slight; active iron corrodes more or less rapidly, its surface darkens and, in some cases, it causes a coloration of the solution. The change from the passive to the active state is affected by a cathodic action which causes a reduction of the protecting oxide layer on the iron. To produce this action only small amounts of zinc or aluminium need be in contact with the iron. When the less noble metal is later removed or dissolved, the iron remains in the active state.

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## MINERAL RESOURCES

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**Bird River Chromite Deposits, Manitoba.** J. D. Bateman. (*Transactions of the Canadian Institute of Mining and Metallurgy*, 1943, vol. 46, pp. 154-183). The author gives an account of the geology of the chromite deposits about 80 miles north-east of Winnipeg. An initial exploration has revealed a total length of about 12,000 ft. of chromite ore varying in width from 6 to 12 ft. There is no massive chromite within any of the deposits. The dense ore consists of closely packed small octahedral crystals of chromite in an interstitial gangue of chlorite and tremolite; normally it contains 20-25% of chromic oxide. The ore can be successfully concentrated by table methods.

**Swedish Geological Investigations—The Search for Ore in Västerbottten.** P. Geijer. (*Teknisk Tidskrift*, 1943, vol. 73, Sept. 11, pp. B73-B78). (In Swedish).

**Coal in Turkey.** F. Gurses. (*American Institute of Mining and Metallurgical Engineers*, 1943, Technical Publication No. 1602). An account is given of the geology of the coal-beds in Turkey and the economic aspects of the coal industry. Extensive deposits of bituminous coal and lignite occur. Between 1923 and 1939 the average annual production was 1,870,000 tons.

## ORES—MINING AND TREATMENT

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(Continued from pp. 1 A-2 A)

**Development of Sink-and-Float Concentration on the Iron Ranges of Minnesota.** G. J. Holt. (*American Institute of Mining and Metallurgical Engineers*, Technical Publication No. 1621 : *Mining Technology*, 1943, vol. 7, Sept.). The author gives a brief account of the sink-and-float ore-concentration process for Mesabi ores as practised by the Cleveland Cliffs Iron Co., using as medium a suspension of ground ferro-silicon (iron 83% and silicon 15%) in water.

**Magnetic Separation Comes into Its Own.** R. L. Manegold. (*Engineering and Mining Journal*, 1943, vol. 144, Aug., pp. 86-88). After reviewing the development of the use of magnets for separating ores in the United States and Canada, the author briefly describes the wet magnetic separation process adopted by the Republic Steel Corporation at Port Henry in New York State.

**The Effect of Heat Treatment on the Magnetic Properties of Iron- and Manganese-Bearing Minerals.** G. G. Bring. (*Jernkontorets Annaler*, 1943, vol. 127, No. 9, pp. 447-490). (In Swedish).

After reviewing the literature on the changes in the magnetic properties of minerals brought about by heating with and without the admixture of a reducing agent, the author reports on tests carried out with various Swedish ores containing manganese, describing the methods used for measuring the magnetic properties. The minerals used were knebelite from Tuna Hästberg, Bastkärn and Stollberg, grünerite from Bastkärn, granite, "*gröna mineral*" (a green, partially converted pyroxene) from Tuna Hästberg, and dolomite from Tuna Hästberg and Klackberg. Knebelite and grünerite became more magnetic and had increased remanence after heating for 2 hr. at 800–900° C. Knebelite from all localities and grünerite are relatively strongly ferro-magnetic. Granite and "*gröna mineral*" are paramagnetic after heating and no coercive force could be detected even after heating up to 900° C. with carbon. The only change in dolomite from Tuna Hästberg was that the manganese content was increased by heating to 900° C. because the carbon dioxide was driven off. An interesting change occurred when Klackberg dolomite, which is higher in iron, had been heated to about 700° C., in that its magnetic susceptibility was increased three to five times, whilst after roasting at higher temperatures the value decreased almost to that at room temperatures. When this dolomite had been roasted with carbon, the magnetic susceptibility rose steadily over the whole temperature range, probably because of the formation of magnetite. Knebelite and grünerite are sufficiently magnetic to be easily attracted in powerful magnetic separators, or to be separated in an alternating-current field. Granite and dolomite could be treated in alternating-current fields of the strength used in these tests. After heat treatment, granite responded somewhat better in powerful magnetic separators. Untreated clean specular iron ore from different districts responded only slightly in powerful direct-current magnetic separators, but quite well in alternating-current separators. A bibliography with 73 references is appended.

**Some Aspects of Sintering Ores.** R. Hay and J. McLeod. (*Journal of the West of Scotland Iron and Steel Institute*, 1942–43, vol. 50, Part VI., pp. 55–64). The authors discuss the mechanism of the formation of sinter and the influence of various factors on sintering. Water additions to a bed of coarse ore particles makes very little difference in the resistance to the passage of air, but with fine material a small water addition increases this resistance; with further additions of water the resistance rapidly falls to a minimum and then increases again. With very fine ore the amount of water to give minimum resistance is very critical. In synthetic sinters the quantity of carbon present in the original mixture is a very important and critical factor, for not only does the carbon supply the necessary heat to bring about the sintering, but it also reduces some of the iron oxide in the ore to ferrous oxide which readily combines with the silica to form fayalite ( $2\text{FeO} \cdot \text{SiO}_2$ ).

Satisfactory sinters were produced from pure ferric oxide made from iron oxalate. Carbon in varying proportions was added to the pure oxide and the mixture heated to various temperatures for various times, both *in vacuo* and in air; in some cases free iron together with ferrous oxide and magnetite was obtained. From a study of polished specimens it appears that ferrous oxide is formed as the first product which is in the liquid state. As the reaction proceeds, small cubes of magnetite separate out from this liquid phase, and these keep on growing as the reactions continue, until all the iron is present as magnetite. This type of change occurs both in air and *in vacuo*, but with the difference that in air more magnetite is produced under a given set of conditions.

## REFRACTORY MATERIALS

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**Dolomite Refractories.** J. H. Chesters. (*Iron Age*, 1943, vol. 152, Aug. 5, pp. 48-53; Aug. 12, pp. 36-89, 150-152). The author discusses some of the binary and ternary systems involving magnesia. Two serious limitations have hindered the development of dolomite brick. One is the tendency of calcined dolomite to "perish" by reacting with moisture in the air to form hydrates; the other is the tendency of  $\beta$ -dicalcium silicate formed in brick-making, or in service, to invert to  $\gamma$ -dicalcium silicate with a 10% increase in volume and the formation of an extremely fine powder. A. H. Jay and L. Bragg have shown that dolomite bricks which formed hydrates contained small amounts of uncombined lime owing to insufficient silica or inadequate firing, whilst those which dusted after use in the open-hearth furnace contained considerable amounts of  $\gamma$ -dicalcium silicate. The manufacture, properties and steel-furnace applications of calcined dolomite (often called "basic"), semi-stabilised and fully-stabilised magnesite-dolomite bricks and of dolomite-chromium bricks are discussed.

**Sillimanite-Chrome Mixtures.** A. A. Chadeyron and W. J. Rees. (*Transactions of the British Ceramic Society*, 1943, vol. 42, Aug., pp. 163-170). Fired sillimanite mixes containing up to 20% of chromic oxide, and 5% and 10% of a South African chromite and an Indian chrome concentrate were tested in a laboratory. The results of slag tests using: (a) An acid open-hearth slag, (b) a basic open-hearth slag, and (c) a hammer scale, indicated a marked increase in the resistance to ferruginous slags with contents of chromic oxide up to 15%. Mixtures of higher chromic oxide content did not show any further increase in slag resistance. The refractoriness-under-load was slightly lowered for mixtures containing up to 15% of  $\text{Cr}_2\text{O}_3$  and appreciably reduced for amounts in excess of this. An improvement in the slag resistance was also found with the products containing chrome ore, but it was less than that

obtained by using chromic oxide ; the refractoriness-under-load was reduced. The spalling resistance of all the test products was high, the thermal expansion was slightly increased by the chromic oxide and chrome ore additions.

**High Temperature Heat Insulation.** G. W. Paterson. (*Refractories Journal*, 1943, vol. 19, Aug., pp. 263-282). The author discusses the principles of heat insulation, the forms in which heat-insulating materials are available, how they are made, and their effects on the fuel economy of furnaces in general. Specific examples are cited of the economies effected by applying insulation to open-hearth steel furnaces. Spalling losses from silica bricks are not as severe with insulation owing to more thorough conversion of quartz into more stable mineral forms. Slag pocket accumulations are also not so great, since the volume and velocity of the products of combustion decrease in the same ratio as fuel consumption decreases.

## FUEL

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(Continued from pp. 2 A-5 A)

**Heat Utilisation in the Steelworks.** R. J. Barratt. (*Metallurgia*, 1943, vol. 28, Sept., pp. 211-214). The author presents and discusses data on the consumption of fuel for coke-ovens, blast-furnaces, open-hearth furnaces, soaking pits, reheating furnaces and boilers. He explains how fuel requirements are calculated and balanced, with two hypothetical examples, one for blast-furnaces and coke-ovens on a 1000 tons of iron per week basis, and the other for a steel plant producing 1000 tons of ingot per week. It is shown that, for low fuel consumption, a composite works is more favourably placed than any separate combinations of its units.

**Heat Recuperation.** (*Machine Shop Magazine*, 1943, vol. 4, Oct., pp. 80-83). The use of metallic recuperators has been limited owing to their high initial cost when they are made of special alloys. A new design of recuperator called the "Thermobloc," which can deal with waste gases at temperatures in excess of 1000° C., is described. It is made in two sizes, 9 × 9 × 12 in. and 9 × 12 × 15 in., with heat-exchanging surfaces of 5 and 10 sq. ft. respectively. The working unit consists essentially of two banks of small-diameter tubes contained in a matrix of cast iron; one bank is disposed vertically in the matrix and the tubes of the other bank are horizontally interlaced between them. On entering the vertical bank of tubes the waste gases are thus split up into a large number of small-diameter streams and present a very large surface area for the release of sensible heat into the horizontal tubes. The rate of heat absorption is intensified by fitting "corebusters" inside the tubes; these are spiral strips which deflect the core of the gas

stream to the tube walls. These recuperators have been successfully applied to hardening furnaces for high-speed steel tools heated by clean producer gas.

**The Rational Preparation of Coal.** R. Lessing. (*Journal of the Institute of Fuel*, 1943, vol. 17, Oct., pp. 15-24). The author points out that, apart from the separation of a portion of ash-forming minerals by cleaning processes, the bulk of coal is submitted to various methods of utilisation in the form of the mixture of components in which it is found underground and mined. It is, however, a highly desirable object of the preparation of coal to separate it into portions of different character, so that collieries could subdivide their products as closely as possible to suit the needs of each class of consumer, and not merely select the coals according to their preponderating qualities for steam, house, coking or gas coal. It is shown how the principal branches of utilisation will be affected by the use of coal components separated according to a comprehensive scheme of preparation.

**The Washing of Pittsburgh Coking Coals and Results Obtained on Blast Furnaces.** C. D. King. (*American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1618 : Metals Technology*, 1943, vol. 10, Sept.). As the deterioration of Pittsburgh coking coals will be accelerated as some of the better grades are worked out and by the extension of mine mechanisation, and as the new seams to be worked are known to be high in sulphur, a study was made of the improvements in the coke produced and the changes in blast-furnace practice which might be required as a result of washing the coals. The high-volatile seam coals from Fayette and Greene Counties were investigated. Washing the coal not only reduced the ash and sulphur in the coke, but also increased the uniformity of the coke quality. The yield of furnace coke was increased by about 3%. The conclusion drawn from comparing data on blast-furnace operation over two test periods, each lasting two months, was that using coke from washed coal was very beneficial because : (1) The daily production of about 800 tons of iron was increased by 8.1%; (2) the coke consumption per ton of iron was reduced by 7.8%; (3) the flux consumption was reduced by 19.9% and the slag volume by 15.2%; and (4) the analysis of the iron was much more uniform.

**Metallurgical Coke.** R. J. Barritt. (*Metallurgia*, 1943, vol. 28, Oct., pp. 267-272). A review of the development of coke-oven design and coke-making practice is presented. Descriptions of beehive ovens, "French" ovens and a modern battery of by-product ovens are given with information on the properties of coking coals, the coke produced and methods of testing coke.

**Gas Producer Flue Cleaning Plants.** R. P. Nuki. (*Iron and Steel*, 1934, vol. 17, Oct. 21, pp. 49-50). The author describes with the aid of diagrams the layout of blowers and pipe-lines for rapidly removing deposits from underground and overhead producer-gas

flues. A saving of fuel is effected, as the flues do not have to be cooled down and entered for cleaning. The maintenance cost of refractory flue and pipe linings is reduced for the same reason, and a very dirty and unhealthy job is eliminated.

**Town's Gas and the War Effort.** W. F. Howell. (*Fuel Economy Review*, 1943, vol. 22, pp. 14-20). The author describes and illustrates numerous examples of applications of gas-fired furnaces in steelworks for ingot and billet heating, heat treatment, &c. Data on gas consumption are cited in several cases.

## PRODUCTION OF IRON

(Continued from pp. 5 A-8 A)

**Sinter and Blast-Furnace Thermal Principles.** C. E. Agnew. (*Steel*, 1943, vol. 113, Oct. 4, pp. 110-114, 128; Oct. 11, pp. 262, 282-288). The use of very high proportions of sinter in blast-furnace charges is discussed in the light of the theories on blast-furnace operation put forward by J. E. Johnson jun. in 1918. The use of sinter, or any other material free from volatile matter, in the furnace burden changes the heat requirements in the shaft in proportion to the percentage of sinter charged, and, unless adjustments are made in the amount of heat delivered to the shaft, the relation between the heat requirements of shaft and hearth will be thrown out of balance and the fuel consumption will increase. Concentration of heat in the hearth can be obtained by a slow combustion rate at the tuyères and a high blast temperature; a high carbon solution loss in the shaft of the furnace is then desirable for concentrating heat in the hearth because it permits the recovery, in the form of heat from the hot blast, of a greater percentage of the B.Th.U. value per lb. of coke than is possible by direct combustion of the coke in the furnace. It is probable that the relation between the dimensions of the hearth and bosh region to those of the shaft should be different for a full sinter burden than they are for a soft ore burden. As sinter is a good conductor of heat, a minimum of time will be required for the sinter to absorb the heat necessary to arrive at the temperature of incandescent carbon, and it is the plane at the upper limit of incandescent carbon in the furnace which determines the size of the hearth and bosh region. This region should therefore be larger and the shaft region smaller than for a soft-ore burden. The use of a full sinter burden and a properly adjusted blowing rate presents the ideal conditions for recovering the thermal value of the exothermic reactions of the shaft region, and it is highly probable that enough heat is generated by those reactions to effect the greater part of the iron oxide reduction, thus leaving all of the heat generated in the hearth free for hearth work.

**Production of Low-Phos. Charging Stock by Direct Reduction.** (Steel, 1943, vol. 113, Aug. 30, pp. 88-92, 102-109). A description is given of the Harman direct reduction process of producing a sinter or pig-iron low in phosphorus and sulphur which is suitable for charging in steel furnaces. It is proposed to apply this to reduce the titanium and vanadium-bearing ores of the Adirondacks. The process has been described by E. S. Harman (*see Journ. I. and S.I.*, 1943, No. II., p. 9 A).

**The Decomposition of Crude Phosphate by Smelting with Soda Slag.** K. H. Hennenberger. (Iron and Steel Institute, 1943, Translation Series, No. 164). This is an English translation of a paper which appeared in *Stahl und Eisen*, 1939, vol. 59, June 1, pp. 62-63 (*see Journ. I. and S.I.*, 1939, No. II., p. 133 A). The process in question was developed for the utilisation of the slags now available in Germany from the desulphurisation of pig iron with soda ash.

**Metal Working in Powder Metallurgy.** C. G. Goetzl. (Wire and Wire Products, 1943, vol. 18, June, pp. 329-330, 355; July, pp. 394-395, 427; Aug., pp. 457-460). The author explains some of the characteristics of parts made by powder metallurgy, describes how tungsten and tantalum wire is made and discusses some tests on bars made from sintered iron and sintered copper powders. After 75% reduction by cold-rolling, sintered electrolytic iron bars had a maximum density of 7.74 g. per c.c. After 50% reduction by hot-forging, a density of 7.85 g. per c.c. was obtained; both the tensile strength (42,000 lb. per sq. in.) and the elongation (27%) were low in comparison with those for soft wrought iron. With increasing reduction up to about 50% by hot forging, the tensile strength, elongation and Brinell hardness all increased. Still further reduction caused a falling-off in these values.

**Powder Metals Find Wide Use.** (Machinist, 1943, vol. 87, Oct. 16, pp. 83-86). Descriptions are given of parts made from powdered bronze, iron-copper and iron by the powder metallurgy process. Nearly all the parts are for bushes and bearings in the automobile industry. Data are presented on their strength, porosity, hardness, weight per cubic inch and expansion.

**Prehistoric and Primitive Iron Smelting. Part II. The Crucible Processes of the East.** E. Wyndham Hulme. (Transactions of the Newcomen Society, 1940-41, vol. 21, pp. 23-30). Descriptions are given of the early iron-smelting processes of China, India, Ceylon and Japan. The primitive processes of Egypt, Central India, Persia and Palestine were dealt with in the first part (*see Journ. I. and S.I.*, 1938, No. II., p. 202A.)

**Henry Cort's Bicentenary.** H. W. Dickinson. (Transactions of the Newcomen Society, 1940-41, vol. 21, pp. 31-47). An account is given of the life of Henry Cort (born 1740, died 1800). Cort took over a forge at Fontley, 6 miles from Gosport, and there developed a process of making malleable iron from cast iron by puddling.

He is best known for his application of grooved rolls to the rolling of wrought-iron bars, which was a very great advance on the slow method with the tilt-hammer. He had extensive dealings with the Portsmouth Dockyard, from which he bought quantities of old mast-hoops and other ship's ironwork which he was able to work up into plates, bars, half rounds and hoops. Cort died a poor man owing to his partner being found to be a defaulter to the Navy for a large sum of money.

**The Use of Cast Iron in Building.** S. B. Hamilton. (*Transactions of the Newcomen Society*, 1940-41, vol. 21, pp. 139-155). About 1755 John Smeaton introduced cast-iron windshafts and gear-wheels into windmills, and from then until about 1830 the use of this material extended in a haphazard manner. The tentative phase ended about 1830, and cast-iron construction became a subject of deliberate and scientific study. The culminating period came about 1850, after which a gradual decline set in. In this paper examples of the use of cast iron in building in the above periods are given with numerous illustrations.

## FOUNDRY PRACTICE

(Continued from pp. 8 A-12 A)

**Casting High Duty Iron.** T. Roberts. (*Mechanical World*, 1943, vol. 114, Oct. 22, pp. 467-468). The author makes recommendations for small foundries which are making castings of high-duty iron for the first time. Brief notes on four methods of producing the iron are given; these are: (1) The straight-mix method, in which the cupola charge is adjusted to produce iron to the required analysis; (2) the duplex method; (3) by inoculation, in which powdered ferro-silicon, or calcium silicide, or some other material is added to the stream of metal on tapping the cupola; and (4) by making ladle additions of suitable materials containing the alloying elements required. Some hints on the placing of risers for alloy-iron castings are given.

**Pours Triplex Steel on Conveyor.** A. H. Allen. (*Foundry*, 1943, vol. 71, Sept., pp. 94-95, 188, 189). The author gives an illustrated description of the melting and casting plant at the new steel foundry of the Ford Motor Co., at Dearborn, Michigan, where steel castings for ordnance and aircraft are made. The triplex process with cupolas, side-blown converters and acid-lined electric-arc furnaces is used. The converters require 4 min. for charging, 20 min. for blowing and 4 min. for tapping; the linings last 30-35 blows. Alloying materials are added to the ladle in which the steel is transferred to the electric furnaces; the latter are used as metal reservoirs holding 10-15 tons of metal each. The steel is tapped at

about  $3000^{\circ}$  F. and loses  $80$ – $100^{\circ}$  F. before being poured into the moulds. A continuously moving conveyor brings the moulds up to the pouring platform. After removal from the moulds the castings are hung on a cooling conveyor which brings them slowly to the fourth floor of the building, where they are trimmed.

**The Production of Air-Cooled Cylinders.** T. H. Taft. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 71, Nov. 11, pp. 199–204). The practice at an English foundry making cast-iron internal-combustion engine cylinders with thin deep cooling fins is described. Congleton silica sand is the basis of all the sand used. Oil sand is used for the facing of all dried moulds, the mixture consisting of 60% of recovered black sand with 40% of new sand, lightly milled to give a medium bond in the green state. The same mixture, milled for a longer period, is applied for making plain body cores and barrel cores. All mixtures contain dextrine 0·75%, linseed oil 0·75% and water 0·25%. Small and medium cores are dried for 1 hr. 10 min. at  $285^{\circ}$  C., and large cores and small moulds for 1 hr. 25 min. at  $285^{\circ}$  C. The physical properties of the sand mixtures are given. Two 24-in.-dia. cupolas are employed to prepare the iron from charges made up of two brands of refined iron and one straight blast-furnace iron. The iron as-cast contains total carbon 3·20%, combined carbon 0·70%, silicon 1·95%, phosphorus 0·60% and manganese 0·75%. The melting rate is 35 cwt. per hr. and the metal/charge-coke ratio is 7·5. Foundry scrap from all sources is 3·5% and return scrap after machining is 1·2%.

**Developments in America in the Centrifugal Casting of Steel.** J. E. Hurst. (Iron and Steel, 1943, vol. 17, Oct., pp. 9–12). The author discusses the position in the United States of the casting of steel by the centrifugal process and describes the plant at different works. In 1942 twenty-two firms used machines with a horizontal axis and fourteen were using vertical spindle machines; some of these machines had metal moulds and others sand moulds and cores.

## PRODUCTION OF STEEL

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(Continued from pp. 12 A–14 A)

**Iron and Steel Industry in India.** (All-India Manufacturers' Organisation : Iron and Coal Trades Review, 1943, vol. 147, Nov. 5, pp. 711–712). The production of iron and steel in India is reviewed. In 1927–28 the total imports of iron and steel into India reached a peak at 1,450,000 tons, and by 1936–37 this had fallen away to 400,000 tons; in the same period Indian production rose from 429,000 to 935,000 tons. The manufacture of acid steel and the addition of a wheel, tyre and axle plant to the works of the Tata Iron and Steel Co., Ltd., mark a new chapter in India's iron and steel

industry. Various works are now producing special billets for shell manufacture, bullet-proof steel, steel helmets, shear blades, spring steel, deep-drawing steel and alloy steel for aircraft, but the productive capacity is still much below requirements and steel is still being imported even for war purposes.

**Precedent Unsualted at Kaiser Steelworks.** J. D. Knox. (*Steel*, 1943, vol. 113, Sept. 27, pp. 72-75, 130-132). Particulars of the new integrated steelworks built by the Kaiser Co., Incorporated, at Fontana, California, which has recently commenced production, are given. The ore, with an iron content of 51%, is brought from San Bernardino County, 176 miles away; the coal comes from Carbon County, Utah, 807 miles away; the limestone is obtained locally. The plant comprises 90 coke-ovens, a blast-furnace producing 1200 tons per day, six 185-ton open-hearth furnaces, a plate mill, a section mill, a merchant bar mill with all the necessary auxiliary equipment. The estimated annual production is 432,000 tons of pig iron, 675,000 tons of ingots and 472,000 tons of finished rolled steel.

**Geneva Steelworks.** (*Iron and Steel*, 1943, vol. 17, Oct. 21, pp. 39-42). A brief illustrated description is given of the new Geneva Steel Works at Provo, Utah, which is now being built by the Columbia Steel Co. The major units of the works are three blast-furnaces, each to produce 1200 tons of iron per day, nine 225-ton open-hearth furnaces, four batteries of coke-ovens and a by-product plant, a slab mill, a semi-continuous plate mill, a section mill, and a 50,000-kW. power-station.

**Proceedings of the Twenty-Sixth National Open-Hearth Conference.** (American Institute of Mining and Metallurgical Engineers, Open-Hearth Conference, Apr. 29-30, 1943). The Twenty-Sixth Open-Hearth Conference of the American Institute of Mining and Metallurgical Engineers was held at Cleveland, Ohio, with L. F. Reinartz as the General Chairman.

After the opening remarks by the General Chairman, the paper by E. G. Wigfield which gained the McKune Award for 1943 was presented; in this the melting practice for producing steel NE 1330 (a 0.30% carbon steel) in a 50-ton basic open-hearth furnace is described (*see Journ. I. and S.I.*, 1943, No. II., p. 152 A). An open discussion on personnel then took place; this dealt mainly with the employment of women in steelworks and the improvement of the health and morale of workers generally. This was followed by two papers on safety precautions when running plants at full capacity, one by J. F. Collins, the other by C. C. Hennessey. The next subjects were refractories and furnace maintenance. After some discussion of furnace-bottom maintenance and basic roofs for open-hearths, L. A. Lambing read a paper on organising the rebuilding of an open-hearth furnace so as to reduce to a minimum the time during which it is off production; several illustrations of the scaffolding and other equipment specially designed for dismantling and

rebuilding are presented. M. F. Yarotsky then described how furnace repairs are planned by the Carnegie-Illinois Steel Corporation, where a schedule is drawn up, based on the average furnace life, so that only one furnace at a time is down for relining in any one of the three shops; an incentive plan covering bricklayers' pay is in operation and has proved beneficial. L. E. Smith next described a procedure for loosening and dragging out in one piece the slag in the slag pockets; these blocks measure  $5 \times 8 \times 13$  ft. and weigh about 60 tons. The Open-Hearth Executive Committee made known the answers to a questionnaire on furnace construction, operation and repairs which were sent in by six works. The design of hot tops for ingot moulds was discussed by G. Soler. A theory of the cause of scabs on ingots and recommendations for preventing their formation were put forward by T. J. Woods (see p. 49 A). Two papers on plant maintenance were presented, J. B. Whitlock describing the procedure adopted by the American Rolling Mill Co., and W. A. Perry that of the Inland Steel Co.

At the Annual Dinner, H. G. Batcheller gave an address on the need for more steel for war purposes and how to obtain it. The subject at the beginning of the second day was control equipment for open-hearth furnaces. Three papers were read on this, namely, "Automatic and Other Control Equipment" by R. A. Lambert, "Combustion Control Instrumentation and Important Factors Relative to Its Operation" by J. M. Brashear, and "The Status of Open-Hearth Controls" by M. J. Bradley. These were followed by discussions on changes in character of fuel oil, the charging of large pieces of scrap, the maintenance of hot-metal mixers, and sampling of steel in the ladle. In the Session on Raw Materials, J. T. MacLeod read a paper on the use of steel turnings in open-hearth and electric furnaces and H. F. Walther described the briquetting of turnings. After an open discussion on turnings, the following papers were presented: "The Use of the Spectrograph to Identify Nonferrous Metals in Scrap" by G. T. Motock, "Experience with the Spectrograph at Inland Steel Company" by T. G. Washburn, and "The Spectrograph and Its Application at Gary Works" by A. D. Beers. E. C. Barringer then presented and discussed statistics on the collection and disposal of scrap. Continuing the Session on Raw Materials, H. L. Allen and F. T. Sisco led discussions on charges with a high proportion of hot metal, and on the use of fluorspar, respectively. In a paper on the controlled desiliconising of pig iron, F. E. Lathe described equipment that it is proposed to erect at Sydney, Nova Scotia, in which silicon, manganese, titanium and vanadium would be slagged off by iron oxide just as rapidly as is done in the converter; the essential feature is a rotating reaction drum 21 ft. long  $\times$  7 ft. 4 in. inside dia. in which intimate contact between the mill scale and the molten iron is obtained. F. L. Toy next described successful trials by the Carnegie-Illinois Steel Corporation in the making of hard dense nodules of ore in cement kilns.

An open discussion followed on methods of reducing the quantities of aluminium and ferro-manganese used in steelmaking.

The Session on Quality took place next. This began with W. A. Saylor giving a description of the new integrated iron and steel plant at Fontana, California, which consists of five 185-ton fixed furnaces and one 185-ton tilting furnace. The session concluded with open discussions on the manufacture of National Emergency Steels, the technique and effect of adding boron, the manufacture of medium-carbon steel, pouring practice for sensitive air-hardening steels, and adding deoxidisers to the last ingots of killed steel to prevent too much reduction of the grain size, or "fading."

The Session on Maintenance of Acid Open-Hearth Furnaces consisted of open discussions on bottom-making and furnace repairs, ladle and pouring practice, and the construction of furnace back walls.

The next session was on Practice and Quality and it opened with a brief discussion of control methods in making acid open-hearth steel. This was followed by a paper in which G. R. Fitterer reviewed recent developments in acid open-hearth practice in Europe. G. E. Herbst gave an account of the working of a heat of manganese-molybdenum steel for making cast armour plate. The effects of hydrogen in steel were dealt with by C. A. Zapffe, who described experiments demonstrating the rapidity of the penetration of steel by this gas and the very high pressure which can be developed; he also discussed the sources of hydrogen and means of eliminating dissolved hydrogen.

**The Heating of Open-Hearth Furnaces with Mixed Coke-Oven and Blast-Furnace Gas.** R. W. Evans. (Iron and Steel Institute, 1944, this Journal, Section I). The principles of flame development are discussed; it is shown that high-temperature flames are the result of rapid combustion. The rôle of the flame in an open-hearth furnace during (1) melting and (2) refining the charge is described, with a note on refining with non-luminous flames; refining with a non-luminous flame renders the process inflexible. Slag foams are next discussed; the foam is due to high surface tension in the slag, which can easily be reduced by the introduction of a more luminous flame—hence foams are due more to the nature of the flame than to that of the slag. Foaming slags react seriously on output and furnace wear.

The development of luminosity in mixed coke-oven and blast-furnace gas flames is due to the cracking of hydrocarbons, and the degree of luminosity that may be expected from a given mixture is shown. The nature of the cracking and of the resulting carbon particles depends on the temperature; the size of particles precipitated affects the degree of luminosity. Loss of calorific value in coke-oven gas owing to preheating is discussed, and it is suggested that it may be more efficient to preheat blast-furnace gas only, injecting the coke-

oven gas cold with tar, &c., as an illuminant. The effect of moisture content is shown theoretically to have an adverse effect on luminosity. Furnace design with particular reference to the gas-port is discussed, with a note on port water-cooling, port slope and gas velocity. Different methods of introducing artificial illuminants are described. Mixed gases require plenty of air. Sloping back walls improve the roof life, but the roof should not be low. The operation of mixed-gas furnaces is dealt with and the instrumentation is described. Dolomite consumption is less in mixed-gas than in producer-gas practice. Metallurgically, mixed-gas furnaces do not oxidise the bath so readily, owing, it is suggested, to free hydrogen in contact with slag hindering the transference of oxygen to the slag. In conclusion, the author suggests that, where the coke-oven gas is lean, it can more efficiently be injected cold with tar as an illuminant. Preheating of the air supply only is then necessary.

**Wartime Scrap Problems.** F. E. Vigor. (American Iron and Steel Institute : Blast Furnace and Steel Plant, 1943, vol. 31, Sept., pp. 1025–1027). The problem of obtaining adequate supplies of scrap for the steelworks in the United States is discussed. Still more attention to proper sorting and the increased use of turning crushers are advocated.

**Steelmaking of the Future.** W. Lister. (British Steelmaker, 1943, vol. 9, Nov., pp. 496–499, 503). The author describes the probable course of the development of steelmaking processes during the next few years. Electric iron reduction furnaces will take the place of blast-furnaces. Smelting 1 ton of ore containing about 55% of iron will require about 818 lb. of coke. The iron thus produced will be restored in "active" mixers which will desiliconise it almost completely. This iron, containing about 1·50% of carbon, will be refined in 50-ton electric finishing furnaces with a lay-out such that 50 tons of steel could be tapped every 45 min. Coke will be made on the steelworks site so that the gas could be utilised for the mixer and soaking pits; alternatively, the coke could be made at the mines and the gas conveyed in pipe-lines over much longer distances than at present.

**Increasing the Yield of Electric Furnaces.** H. F. Walther. (Metal Progress, 1943, vol. 44, July, pp. 111–112). The author makes recommendations on methods of increasing the production of electric steel furnaces. These relate, in general, to improving the form of scrap and to more rapid charging. Medium and low-carbon steel turnings prepared by washing, briquetting and roasting form one of the best types of scrap, and this practice should be greatly extended.

**The Origin, Definition and Prevention of Scabs.** T. J. Woods. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1616 : Metals Technology, 1943, vol. 10, Sept.). The author reports on a study of the formation of scabs on ingots measuring 24 × 52 × 82 in. of semi-killed steel for rolling plates.

He found that scabs are not due to individual splashes on the ingot surface, but that they are either pieces of a shell that is present near the bottom of all top-cast ingots, or parts of a veneer or skin that may be present on any part of an ingot not properly poured. Tests with tar-coated, pitch-coated and uncoated ingot moulds showed that the coating was not a factor in scab formation. The way the first splashes of metal from the stream striking the mould stool form the shell round the base of the ingot is explained in detail. The formation of scabs is prevented if the nozzle is large enough for the level of the liquid to rise in the mould sufficiently rapidly to reach the top of the shell before the latte has become too cold and oxidised.

## FORGING, STAMPING AND DRAWING

(Continued from pp. 14 A-15 A)

**Cast Dies for Forging Shells.** P. Attenborough. (*Metals and Alloys*, 1943, vol. 18, Aug., pp. 287-291). The author gives examples of the successful application of Meehanite cast iron for dies for forging shells and bomb-cases. In many instances the cast iron has given better service than nickel-chromium-molybdenum air-hardening steel.

**Forging Shell at Ambridge.** A. F. Macconochie. (*Steel*, 1943, vol. 113, Aug. 30, pp. 82-86, 95). The author describes the sequence of processes in the pierce-and-draw method of forging shells from billets at the Spang-Chalfant Division of the National Supply Co., Ambridge. Two 320-ton vertical presses and one 75-ton horizontal drawing-bench are used.

**Forging and Heat Treating 90-mm. Guns.** G. E. Stedman. (*Heat Treating and Forging*, 1943, vol. 29, Aug., pp. 384-388). The author describes the forging and heat-treatment processes developed by the Wheland Company of Chattanooga, Tennessee, to manufacture barrels and fittings for 90-mm. guns.

**Forging and Heat Treatment of Gun Barrels.** (*Machinery*, 1943, vol. 63, Oct. 28, pp. 483-486). The forging and heat-treatment practice at the Titusville Iron Works in Pennsylvania, where 37-mm. and 57-mm. gun barrels are made, is described and illustrated. The billets are heated to about 2200° F. in oil-fired furnaces for forging under a 6000-lb. steam hammer; they are transferred from the hammer to steel boxes and completely embedded in fuller's earth, where they remain for 10 days, to ensure complete annealing. For heat treatment, batches of thirty 37-mm. barrels or sixteen 57-mm. barrels are suspended from a "spider" casting. The treatment consists of holding for 8 hr. at 1650° F., cooling in still air to 800° F., reheating to 1600° F., holding at 1600° F. for 8-10 hr.,

quenching in oil to 200–250° F., reheating to 1000–1100° F., holding for 10 hr., and cooling in air. The entire heat treatment takes about 72 hr.

**Steel Cartridge-Cases for 37-mm. Shell.** C. L. Patterson and H. R. Turner. (*Machinist*, 1943, vol. 87, Nov. 13, pp. 113–124). The authors give a detailed and illustrated description of the sequence of processes in the pressing and heat treatment of steel cartridge-cases 37-mm. in dia. × 9 in. long from blanks 3·375 in. dia. × 0·420 in. thick.

**A Simple Hydropress Formability Test for Sheet Metals.** G. C. Barber. (*Mechanical Engineering*, 1943, vol. 65, Sept., pp. 643–646). The author describes and illustrates sheet-metal pressings from a standard die which was designed so as to subject the metal in one operation to different degrees and types of forming. For example, parts of the metal being tested are elongated by 9%, 14% and 23%, and a flange is formed along one side with a radius of curvature varying from  $2\frac{1}{2}$  in. to 25 in. The deformability of sheets of different metals can be rapidly determined by comparative tests with this die.

**Design of Cold-Headed Parts.** H. Chase. (*Metals and Alloys*, 1943, vol. 18, Aug., pp. 292–297). The author discusses the advantages and limitations of the cold-heading process. The raw material is commonly limited to "wire" from  $\frac{1}{8}$  to 1 in. in dia. and up to 7 in. long. Very small rivets are often made by cold-heading, but when the shank is to be threaded it may be cheaper to produce parts below  $\frac{3}{16}$  in. in dia. on screwing machines. With ductile carbon steel, a three-blow header can upset a length of stock equal to about six times its diameter, but the head or flange produced is limited to three or four times the stock diameter, and the head volume to that of a length of stock equal to four diameters. Ductility is the primary requisite for cold heading, and this calls for steels relatively low in sulphur. Among the rules given for cold-heading are the following : (a) Never specify a square inside corner or sharp junction between head or flange and shank if a small radius will meet requirements ; (b) permit rolled threads to be supplied whenever possible ; (c) when a taper is required on any part of the shank, the larger diameter must be nearer the upset end than the smaller diameter ; and (d) when a shank must have a portion not circular in section, minimise the length of this portion and do not specify sharp corners.

**A Chronology of Wire and Wire Products.** F. R. Morral. (*Wire and Wire Products*, 1943, vol. 18, Aug., pp. 451–454). The author presents a chronology of the history of wire-making from the earliest times up to the present day.

## ROLLING-MILL PRACTICE

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(Continued from pp. 15 A-17 A)

**Preventative Maintenance Keeps Steel Mills Motors Running.** M. J. Wohlgemuth and W. W. McCullough. (*Iron and Steel Engineer*, 1943, vol. 20, Sept., pp. 98-107). The authors make recommendations on the maintenance of electric motors in steel-works and present specimens of useful inspection schedules and "trouble correction" charts for A.C. and D.C. motors.

**Unified Drives Increase Rod-Mill Production.** F. R. Grant and G. L. Beaver. (*Steel*, 1943, vol. 113, Sept. 6, pp. 120-122, 151, 152). The authors describe a rod mill which has recently been put in commission at Pittsburg, California. The mill comprises nine roughing stands, six intermediate stands and six finishing stands. Three strands can be rolled simultaneously through the entire mill. Billets 30 ft. long form the raw materials and, when the leading end emerges from the last stand, two-thirds of the original billet is still in the furnace. For power application the mill is divided into nine groups of stands, each driven by an adjustable-speed D.C. motor. The speed relationships between the different groups can thus be changed quickly and easily, so that a great variety of products can be rolled.

**Heavy Gun Tubes from Seamless Tubing.** (*Iron Age*, 1943, vol. 152, Aug. 12, pp. 74-79). In a series of nineteen illustrations with explanatory titles a description is given of the process developed by the Timken Roller Bearing Co. for the rapid manufacture of 75-mm. gun barrels from solid steel bars. The bar is pierced in a horizontal piercing mill in 15 seconds. One end is heated by the induction method prior to forming the breech in an upsetting machine. Loops are welded on the ends of the barrels so that they hang vertically from an overhead conveyor, which carries them through the heat-treatment furnace.

**Control of Steel-Mill Auxiliaries.** (*Iron and Coal Trades Review*, 1943, vol. 147, Nov. 5, pp. 717-718). The photo-electric tube uses energy from light rays to free electrons from the cathode, which are then attracted to the anode, resulting in a small current flow of minute proportions. The energy released is amplified and passed through a photo-electric relay, which may be made to close a power circuit for carrying out various operations. Examples of applications of photo-electric tubes for auxiliary equipment in rolling mills are given. These include controlling the fuel gas supply to a skelp furnace in a tube mill from the temperature of the skelp being rolled, controlling a sheet catcher, and detecting holes in tinplate.

## HEAT TREATMENT

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(Continued from pp. 17 A-19 A)

### **Casehardening Large Gears with High-Frequency Current.**

G. C. Riegel. (*Metal Progress*, 1943, vol. 44, July, pp. 78-83). The author describes the process developed by the Caterpillar Tractor Co., Peoria, for induction case-hardening the teeth of gear-wheels 25·7 in. in dia. with a 5-in. face, which are now made of 0·45% carbon steel instead of a 3·5% nickel steel.

### **Local Case-Hardening.** L. G. Whybrow Palethorpe. (*Engineer*,

1943, vol. 176, Nov. 19, pp. 403-404). There are three methods of selective case-hardening, namely, protection of the area required soft by clay or a proprietary compound, protection by electro-plating with copper, and by leaving additional stock on the area required soft and removing this after carburising but prior to hardening. Generally speaking, the use of clay is not satisfactory. Copper affords protection against pack carburising, gas carburising and salt-bath carburising. The thickness of copper deposit required varies with the time of immersion in the cyanide bath from 0·0005 in. for 1 hr. to 0·002 in. for 4 hr. immersion. To leave additional stock on the part is the most efficient method, but is often impracticable.

### **Sodium Cyanide for Carburising.** L. G. Whybrow Palethorpe.

(*Chemical Age*, 1943, vol. 49, Nov. 6, pp. 469-473). The results obtained when case-hardening steel in sodium-cyanide baths are discussed. Originally, 60% sodium cyanide baths were used, but the tendency now is to reduce the cyanide content to 12-20% and add catalysts such as calcium cyanide, alkaline earth chlorides, or polymerised hydrocyanic acid. Cases from these new baths contain a little more carbon and much less nitrogen. Penetration is more rapid in the catalysed baths and the case is less brittle, owing to the nitrogen content. Selective carburising is carried out either by leaving an additional  $\frac{1}{8}$  in. of stock where necessary, which is machined off afterwards, or by copper-plating the parts to be left soft. Although carburising power is not in linear relation to bath strength, any appreciable fall in the latter undoubtedly affects both penetration and the quality of the case. The rate of fall of cyanide content is proportional to the time at the operating temperature; the volume of work put through has a negligible effect. Decomposition can be arrested somewhat by restricting the air supply by sprinkling graphite or plumbago on the surface of the melt.

### **Separately Prepared Furnace Atmospheres. Parts I., II., and III.**

C. E. Peck. (*Industrial Heating*, 1943, vol. 10, Mar., pp. 336-342, Apr., pp. 479-482; June, pp. 789-804). The methods of producing the following atmospheres for bright annealing and bright hardening are described : (1) Lean Exogas, a completely burned

fuel gas, slightly reducing ; (2) rich Exogas, a partially burned fuel gas with medium reducing properties ; (3) lean Endogas, a partially cracked fuel gas ; (4) Endogas, a fully cracked fuel gas ; (5) lean Monogas, this is lean Exogas with the carbon dioxide and moisture removed ; (6) rich Monogas, this is rich Exogas with the carbon dioxide and moisture removed ; (7) Ammogas or dissociated ammonia ; (8) rich combusted Ammogas or partially burned dissociated ammonia ; (9) lean combusted Ammogas or completely burned dissociated ammonia.

**Developments in Continuous Gas Carburizing.** R. J. Cowan. (Steel, 1943, vol. 113, Sept. 13, pp. 96, 118-126 ; Sept. 27, pp. 104-105, 113). Developments in continuous gas-carburising furnaces and procedure since 1931 are reviewed ; the problems of finding suitable alloy steels for the trays and furnace equipment, preventing carbon deposit on the work, controlling the composition of the atmosphere and the carbon content of the case, and designing suitable muffles are discussed first, and this is followed by some particulars of three major developments. The first is the adoption of "CG" gas containing butane and propane ; the second is the construction of the "RX" generator. Precise details of the composition of this gas and the operation of the generator are not given. The third is the design of the carburising furnace heated by radiant tubes and fitted with four lines of independent muffles, each with its own pusher and timing mechanism, so that parts of different size, requiring different carburising times, can be worked through the furnace at different speeds.

**Gas-Hardening of Rail Heads.** Yu. Grdina and N. Shubina. (Iron and Steel Institute, 1943, Translation Series, No. 163). This is an English translation of a paper which appeared in Stal, 1940, No. 10, pp. 40-44. See Journ. I. and S.I., 1942, No. II., p. 62 A.

**New Forced Convection Heat Treating Furnace.** L. H. Remiker. (Australasian Engineer, 1943, vol. 43, Aug. 7, p. 20). A brief description of a vertical cylindrical heat-treatment furnace with which temperatures up to 1750° F. can be obtained is given. It is known as the "Super-Cyclone," and is made in several standard sizes up to 72 in. in dia.  $\times$  84 in. deep. Heating is by gas, oil or electricity, and heat is rapidly transferred to the charge by a circulating fan in a separate chamber. Long pieces, such as gun forgings, are suspended from a special fixture and are heat-treated without distortion.

**A Study of the Nitriding Process. I. Effect of Ammonia Dissociation on Case Depth and Structure.** C. F. Floe. (American Society for Metals, Oct., 1943, Preprint No. 16). The depth and microstructure of nitrided cases produced in steel by atmospheres consisting of ammonia and proportions of dissociated ammonia varying from 15% to 85% after treatment for periods of 5-100 hr. were studied. The steel used contained carbon 0.34%, chromium 1.30%, aluminium 1.24% and molybdenum 0.17%. Heat-treated

specimens  $\frac{1}{2} \times \frac{1}{2} \times 4$  in. were prepared. The case formed consisted of two layers, an outer white layer which was very brittle, but had a high corrosion resistance, and an inner layer about ten times as thick in which most of the special elements, but not the iron, had been converted into nitrides. For all degrees of dissociation up to 65% the white layer, consisting largely of  $\text{Fe}_2\text{N}$ , formed shortly after the start of the process. The depth of this decreased with increasing proportions of dissociated ammonia. The depth of the second layer remained practically constant for a given nitriding time regardless of the degree of dissociation up to 65%. At 85% dissociation very little white layer formed. By first nitriding at 30% dissociation for a short period, the dissociation may be allowed to increase to as high as 85% with no sacrifice in case depth. A considerable saving in ammonia may be effected by nitriding at high degrees of dissociation but the equipment must provide for thorough circulation of the gas to prevent "dead" zones from forming where the degree of dissociation is too high for effective nitriding.

**Electric Furnaces for Heat Treatment of Metals.** V. O. Cutts. (G.E.C. Journal, 1943, vol. 12, Aug., pp. 186-191). Some modern British electric heat-treatment furnace installations are described. These include : (1) Three vertical cylindrical furnaces for nitriding cylinder liners for aero-engines ; (2) a 100-kW. continuous roller-hearth furnace for refining and hardening gears ; (3) a 180-kW. chain-conveyor furnace for heating aluminum alloy billets ; (4) a set of three electrode-type salt-bath furnaces for hardening high-speed steel ; and (5) a 40-kW. low-temperature salt-bath furnace.

**Pressure Quenching Subsequent to Heating Prevents Distortion in Steel.** (Steel, 1943, vol. 113, Oct 11, p. 180). A short description, with an illustration, is given of a quenching machine in which batches of steel parts coming from a hardening furnace are pressed by a movable lower platen against a fixed upper platen, while a high-pressure water spray is directed at both sides of the material for about one minute.

**Quenching and Hardenability of Hollow Cylinders.** J. H. Hollomon and C. Zener. (American Society for Metals, Oct., 1943, Preprint No. 1). An extension of Grossmann's method is used to calculate the diameter of the solid steel cylinder, which, when quenched in a given medium, will have the same hardness at the centre as the minimum hardness in the wall of a hollow cylinder quenched in the same medium. Grossmann's method has been explained previously (see Journ. I. and S.I., 1942, No. I., p. 243 A).

**Rates of Cooling in Blocks and Cylinders.** C. B. Post and W. H. Fenstermacher. (American Society for Metals, Oct., 1943, Preprint No. 2). Cooling rates at the centre of cylinders, bars and slabs of different lengths and thicknesses when quenched in oil were determined experimentally in degrees Fahrenheit per second at 1300° F. The data obtained showed that the effect of the length on the cooling

rate through  $1300^{\circ}$  F. at the centre of cylinders and bars is negligible until the length becomes almost equal to the radius or to the smallest of the cross-section dimensions. A method is outlined for computing the cooling rates at different positions across sections of bars, cylinders and blocks. The calculated rates are compared with the data obtained by several standard methods of testing hardenability.

**An Evaluation of Quenching Oils.** E. K. Spring, P. T. Lansdale and C. W. Alexander. (American Society for Metals, Oct., 1943, Preprint No. 3). A study was made of the quenching rates and physical properties of various quenching oils. The data obtained indicate that the difference between the cooling rates, using new and used oils, are negligible. There is an optimum oil temperature which produces the maximum cooling rate at the nose of the S-curve. Warming the oil has the desirable effect of retarding the cooling rate in the region of the transformation to martensite. The cooling rates obtained with mineral and animal oils are similar. The slight difference between the cooling rates obtained with light and with heavy oils can be compensated by adjusting the oil temperature. The most important points in the selection of a quenching oil are to ensure that the flash point is sufficiently high so as not to be dangerous, and that the cost in terms of the weight of steel quenched under normal operating conditions is an economic one.

## WELDING AND CUTTING

(Continued from pp. 19 A-20 A)

**The Measurement of Cooling Rates Associated with Arc Welding and Their Application to the Selection of Optimum Welding Conditions.** W. F. Hess, L. F. Merrill, E. F. Nippes jun., and A. P. Bunk. (Welding Journal, 1943, vol. 22, Sept., pp. 377-S-422-S). This paper constitutes the First Report on investigations undertaken at the Rensselaer Polytechnic Institute under the general supervision of A. B. Kinzel in which the weldability of steels for the fabricating of tanks, gun mountings and other war material was evaluated by constructing cooling curves associated with a variety of welding conditions, plate thicknesses and plate temperatures. Temperatures were obtained by thermocouples and the maximum hardness of the heat-affected zone was determined for the first and last passes of butt and fillet welds in low-carbon ship-plate steel  $\frac{1}{4}$ ,  $\frac{3}{8}$ ,  $\frac{1}{2}$ ,  $\frac{5}{8}$ ,  $\frac{3}{4}$ ,  $\frac{7}{8}$ , 1 and  $1\frac{1}{2}$ -in. thick. Cooling-rate data are tabulated for various initial plate temperatures in the  $37-400^{\circ}$  F. range. The only factors which need be considered as affecting the cooling rates of welds are the energy input in joules per inch, the plate thickness and initial temperature, and the design of the joint. The electrode size used with a given energy input also affects the

cooling rates, the larger electrode causing slower cooling. The cooling-rate data obtained are equally applicable to A.C. and D.C. welding. First-pass cooling rates in butt welds were considerably lower than top-pass cooling rates. In  $\frac{1}{2}$ -in. plate the cooling rates were much higher near the surface of the plate at the edge of the weld than beneath the weld, particularly for low energy inputs. A study of the tempering effects at low temperatures was made using thin specimens, quenched in a salt bath at  $400^{\circ}$  F., and held for different periods. A significant improvement in the ductility of almost completely martensitic specimens held at  $400^{\circ}$  F. for periods of the same order as for preheated welds, was observed. This tempering effect is only important when a significant amount of martensite has been produced by the welding conditions.

**Mechanical Properties of Arc-Welded Chromium-Nickel Steel at Low Temperatures.** V. S. Chernyak, Z. I. Golubeva and I. A. Steinberg. (Avtogennoe Delo : Welding Journal, 1943, vol. 22, Sept., pp. 437-S-438-S). The results of tensile and impact tests at  $+20^{\circ}$ ,  $-40^{\circ}$ ,  $-75^{\circ}$  and  $-183^{\circ}$  C. on weld metal and parent metal of welded and unwelded 18/8 stainless steel plates are presented. The tensile strength of the weld metal increased from 97,000 to 156,000 lb. per sq. in. on lowering the temperature from  $+20^{\circ}$  to  $-183^{\circ}$  C. The impact strength of the parent metal in the unwelded state remained the same at all the above temperatures, but for welded specimens it decreased by 50% on reducing the temperature to  $-183^{\circ}$  C.

**Pressure Welding of Heavy Tubing.** W. G. Wood. (Iron Age, 1943, vol. 152, Sept. 23, pp. 56-58). Brief particulars of a process of pressure butt welding a steel tube  $6\frac{1}{8}$  in. in outside dia. by  $\frac{5}{16}$  in. wall to make an aircraft landing-gear strut are given. Heat is applied to the joint by a ring of small oxy-acetylene burners, and when the metal becomes plastic, pressure is applied which thickens the metal before the actual welding takes place.

**Flash-Welding of Alloy Steels.** H. W. G. Hignett and G. Mayer. (Welding, 1943, vol. 11, Sept., pp. 399-406). While a wide tolerance is permissible in the conditions governing the flash-butt welding of mild steel, for alloy steels the optimum range of conditions for each operation is quite narrow. Some results obtained by research by the Mond Nickel Company are quoted. Flash-welded joints in a variety of alloy steels gave tensile strengths, after heat treatment, equal to those of unwelded steels, but, unless the correct welding conditions were obtained, the ductility was far from satisfactory. Tests on specimens of a manganese-molybdenum steel, machined from welded bars after heat treatment, showed that, whereas welds in which the heat-treated zones were restricted were characterised by low ductility, when the heat input was controlled to give a less localised heated zone, the ductility was improved and complied with the conditions specified. A certain minimum upset must be employed to squeeze out molten metal and non-metallic impurities

and to provide a weld free from cavities, but excessive upsetting is detrimental.

**A Study of the Effects Caused by Arc Welding upon Axially Loaded Structural Steel Bars.** J. Neustadt, G. D. Lodwick and D. P. Schultz. (Welding Journal, 1943, vol. 22, Aug., pp. 353-S-361-S). An investigation in which a comparison was made of the stress-strain curves for  $1\frac{1}{4}$ -in. dia. steel bars, some in the as-received state, and others having a washer 2 in. in dia.  $\times \frac{3}{8}$  in. thick welded at the centre of a 10-in. gauge length is reported; welds were made with no load on the bar, with a tension load of 30,000 lb., and with a compression load of 30,000 lb. on the bar. The elastic moduli were the same both before and after welding, whether the bars were loaded or not. The yield points and ultimate strengths were approximately the same regardless of loading conditions. Bars welded with no load applied had limits of proportionality slightly less than those of all the other bars. The percentage elongation on 8 in. was slightly less for bars welded under a tensile load than for standard bars (*i.e.*, bars welded with no applied load). The deformations of bars due to welding are closely related to the heat input, and the deformation becomes more sensitive to changes in the heat input with increasing load.

**Factors Affecting the Strength of Welded Joints.** R. L. Swan. (Welding, 1943, vol. 11, Oct., pp. 453-455). The author discusses the design of welded joints between flat bars and plates, and between angles and plates, indicating the best positions to make the welds in order to offer the maximum resistance to stresses in various directions.

**Alternating Current Welding in the Steel Industry.** E. Steinert and W. W. Reddie. (Iron and Steel Engineer, 1943, vol. 20, Aug., pp. 45-50). The author discusses the advantages of welding with alternating current and presents data on the characteristics of welding transformers of different capacity.

**Welding Rolled to Cast Steel.** W. J. Thaw. (Mechanical World, 1943, vol. 113, June 25, pp. 687-688). The technique for welding a steel casting with a medium carbon content to a mild steel plate is described.

**Builds Welded Blast Furnace in Eight Months.** R. F. Fey. (Steel, 1943, vol. 113, Sept. 20, pp. 144-150, 168-170). A blast-furnace to produce 1000 tons of iron per day, with its stoves, gas-cleaning plant, mains and other equipment, was recently erected for the Weirton Steel Co., in eight months by welding. Details are given, with numerous diagrams, of the erection procedure, the design of all the welds and the welding technique adopted.

**Fabricating Steel Coke Oven Doors.** H. A. Immisch. (Steel, 1943, vol. 113, Aug. 2, pp. 113-114, 138, 139). The author describes the technique adopted at a coke-oven plant to fabricate steel coke-oven doors by welding. The design of the door is described and illustrated. Trainee welders were employed. To facilitate the welding the plates and angles were mounted in two circular plates

22 in. in dia. having the centres cut out to the shape of the door section. These circular plates rested on two beams, and the door could thus be turned to any desired position.

**Adaptation of Welded Steel to the Paper Machine.** R. S. Conabee. (*Welding Journal*, 1943, vol. 22, July, pp. 504-512). The author describes the application of welding in the construction of modern paper-making machinery. Welding has enabled stronger and lighter machines to be built.

**Working Out Techniques for Welding Armor Plate.** E. G. Biederman. (*Welding Journal*, 1943, vol. 22, July, pp. 516-519). *See Journ. I. and S.I., 1943, No. II., p. 22 A.*

**New Tools from Scrap High Speed Steel.** U. F. T. Norris. (*Journal of the Institution of Production Engineers*, 1943, vol. 22, Aug., pp. 265-272). The author describes the organisation of the high-speed tool-steel reclamation department at Vauxhall Motors, Ltd. The two principal methods in use are the flash-butt welding of high-speed steel ends to high-carbon steel shanks of the same section, and the furnace brazing of small tips to high-carbon steel shanks. Other applications of butt welding are to the manufacture of end-mills, spot facing cutters, counter-bores and rivet snaps.

**Cause and Cures of 14 Common Welding Troubles.** C. H. Jennings. (*Welding Journal*, 1943, vol. 22, Sept., pp. 712-715; *Steel*, 1943, vol. 113, Sept. 20, pp. 128-132). A table with particulars of fourteen different faults and difficulties which arise in electric welding is presented. An illustration of each and the steps to take to overcome them are given.

**Investigation of the Lateral Distortion Produced in Mild Steel Plates by Oxyacetylene Cutting.** C. C. Osgood. (*Welding Journal*, 1943, vol. 22, July, pp. 308-S-316-S). An investigation of the distortion of square mild steel plates, ranging from  $7 \times 7$  in. to  $20 \times 20$  in. and from  $\frac{3}{8}$  to  $\frac{1}{2}$  in. in thickness, caused by making one or more oxy-acetylene cuts from one edge in lines parallel to the adjacent edges for different distances across the plate was carried out. The position of the commencement of the cut was also varied. The distortion caused the cut to open, and the amount of this movement was measured by an extensometer held between two arms clamped to the plate. From the readings obtained a formula was developed which enables the amount of distortion for any length and position of cut to be predicted.

## PROPERTIES AND TESTS

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(Continued from pp. 25 A-30 A)

**High Speed Testing of Mild Steel.** J. H. Hollomon and C. Zener. (*American Society for Metals*, Oct., 1943, Preprint No. 13). The effects of high rates of strain on the shape of stress-strain curves when testing steel are discussed. Data in the literature

on the variation of the tensile properties of mild steel obtained at strain rates in the ranges of ordinary tensile testing machines are plotted and the curves extrapolated to high strain rates. From this it is deduced that in mild steel the yield strength becomes equal to the tensile strength at rates of strain between 1 in. and 10,000 in. per sec.

**Progress in Micro-Testing.** D. W. Rudorff. (*Metallurgia*, 1943, vol. 28, Oct., pp. 273-277). Details are given of methods of testing developed by P. Chevenard and reported in *Revue de Métallurgie*, 1942, vol. 39, p. 66, for determining the thermo-elastic properties of metals and for making micro-tensile, micro-shear and micro-torsion tests and high-temperature creep tests. In all cases the movement of the specimen is transmitted to a mirror and the movement of a reflected beam of light is recorded on photographic paper.

**Heat Treatment Effect on the Torsion Impact Properties of Meehanite.** C. R. Austin and M. M. Lipnick. (*Iron Age*, 1943, vol. 152, Oct. 7, pp. 54-55). The results of torsional impact tests on specimens of alloyed and unalloyed Meehanite cast iron after hardening and tempering are presented. The specimens were heated to 1550° F., quenched to 300° F. in oil and tempered at temperatures in the 400-1200° F. range. With unalloyed specimens the impact strength decreased fairly steadily with increasing tempering temperature to 725° F.; in the 725-825° F. range there was a sharp recovery, but at still higher temperatures the impact strength decreased again. For alloyed Meehanite the impact strength decreased steeply with increasing tempering temperature up to 400° F., remained steady in the 400-725° F. range, increased sharply in the 725-825° F. range, and remained fairly steady in the 825-1100° F. range.

**The Effect of Heat Treatment and Carbon Content on the Work Hardening Characteristics of Several Steels.** J. H. Hollomon. (*American Society for Metals*, Oct., 1943, Preprint No. 14). The true stress-strain curves for a low chromium steel, a low nickel-molybdenum steel and two plain carbon steels were obtained by tests in a Riehle, beam-type, tensile testing machine. From a study of the properties in the plastic range it was seen that the rate of work-hardening increases with increasing initial tensile strength whether due to heat treatment or to a higher carbon content. The addition of nickel raised the rate of work-hardening.

**The Strain Ageing of Killed Low-Carbon Steel, with Particular Reference to the Effect of Titanium.** G. F. Comstock. (*American Society for Testing Materials: Sheet Metal Industries*, 1943, vol. 18, Sept., pp. 1527-1534; Oct., pp. 1723-1730). The strain-ageing of heat-treated specimens cut from forged bars of killed low-carbon steel melted in a small induction furnace was studied by six methods, including comparison of the yield point, and noting the changes in impact value, hardness and damping capacity on

ageing after straining. Results by the damping method were found to agree with those obtained by the yield-point method, but the impact and hardness methods did not classify different steels in this way. Deoxidising these steels with aluminium was effective in preventing the kind of strain-ageing revealed by impact tests, but its influence on the kind shown by yield-point tests was slight. The effect of nitrogen was negligible in these killed steels. Titanium, if present to the extent of at least 4·5 times the carbon content, was effective in preventing strain-ageing as determined by all the methods. Such steel does not have a real yield point whether normalised, annealed, or strained and aged. The nitrogen content of killed low-carbon steels (up to 0·015% in solution or 0·02% total) does not affect to an important degree the susceptibility to strain-ageing.

**Endurance of Machines under a Few Heavy Loads.** J. O. Almen. (*Metal Progress*, 1943, vol. 44, Sept., pp. 435-440). It is shown that, for certain machine parts, the slope of the *S/N* curve (stress/number-of-cycles in fatigue tests) is more useful for design purposes than the endurance limit. The paper is a continuation of an earlier one entitled "The Useful Data to be Derived from Fatigue Tests" (see p. 27 A). The examples include the use of data from fatigue tests on automobile rear axle gears and on ball and roller bearings. The slope of the fatigue curve varies with the stress range as well as with the stress concentration. A three-dimensional diagram of the modified Goodman diagram by Moore and Kimmers is reproduced. The front face of this diagram shows the ordinary *S/N* curves for complete reversals of stress; the back face is an *S/N* diagram for zero stress range, i.e., a static stress; and a section half-way between these is for a stress range of zero to maximum. The front face is therefore applicable for crankshafts and the back face for properly tightened bolts. Laboratory tests should produce failures in approximately the same number of stress cycles as that producing service failures, and this requires that distinction is made between stress under normal operation and the relatively infrequent overloads that cause failure.

**The Effect on the Endurance Limit of Submerging Fatigue Specimens in a Cold Chamber.** O. H. Henry and A. Stirba, jun. (*Welding Journal*, 1943, vol. 22, Aug., pp. 372-S-373-S). The results of fatigue tests on specimens of welded and unwelded mild steel plate (carbon 0·20%, manganese 0·65%) at six temperatures in the range 20° C. to -70° C. are reported. The procedure was that described by O. H. Henry and T. D. Coyne (see *Journ. I. and S.I.*, 1942, No. II., p. 218 A). Both welded and unwelded specimens showed an increase in endurance limit with decreasing temperature. The break in the stress-temperature curve was sharper at the higher temperatures than at the lower ones.

**Hardenability.** J. G. Ritchie. (*Australian Institute of Metals : Australasian Engineer*, 1943, vol. 43, July 7, pp. 14-16, 37-43 ;

Aug. 7, pp. 14-15, 37-43). The author discusses methods of determining the hardenability of a steel, explaining in detail Grossmann's method and the Jominy end-quench test. These methods have been applied to determine the effects of chemical composition, grain size of the austenite, hardening temperature, holding time and initial structure on the hardenability of steel. With regard to composition, an example of the use of Grossmann's multiplying factors for calculating the effect of alloying elements and impurities on the "ideal critical size" is given (*see Journ. I. and S.I.*, 1942, No. II., p. 219 A).

**The Effect on the Hardenability of Small Additions of Chromium and Molybdenum to a Grain-Size-Controlled 0·9% Nickel Steel.** W. Steven. (Iron and Steel Institute, 1944, this Journal, Section I). Nineteen grain-size-controlled steels (American Society for Testing Materials grain size  $6\frac{1}{2} \pm 1$ ) of the following foundation analysis (by weight) were made by the crucible process: Carbon  $0\cdot33 \pm 0\cdot04\%$ ; manganese  $0\cdot60 \pm 0\cdot10\%$ ; silicon  $0\cdot21 \pm 0\cdot04\%$ ; sulphur  $0\cdot039 \pm 0\cdot007\%$ ; phosphorus  $0\cdot020 \pm 0\cdot004\%$ ; and nickel  $0\cdot89 \pm 0\cdot03\%$ . The effect of simultaneous additions of molybdenum and chromium to this steel over the range zero to 0·6% of molybdenum and 0·2-8% of chromium was determined by the Jominy end-quench method. The results indicate that the hardenability of these steels does not vary as the quenching temperature is altered from  $850^\circ$  C. to  $880^\circ$  C. or as the time of soaking at the quenching temperature is increased from 20 minutes to 60 minutes. When the hardenability of this series of steels is expressed in terms of Grossmann's ideal critical diameter ( $D_\infty$  inch) the following relation exists between the hardenability and the weight percentages of chromium and molybdenum:

$$D_\infty = 2\cdot36 \text{ Cr}^2\text{Mo} + 2\cdot00 \text{ CrMo} + 0\cdot60 \text{ Mo} + 1\cdot70 \text{ Cr} + 1\cdot31.$$

This equation enables the hardenability of any steel within the range of analysis investigated to be calculated from its chemical composition. Ideal critical diameters calculated from analysis figures by Grossmann's method agree only approximately with the experimental results. By using the above equation, data are tabulated indicating the percentages of chromium and molybdenum required to produce a steel of a given ideal critical diameter, and three iso-hardenability diagrams have been drawn giving the critical diameters corresponding to an ideal quench, a water-quench and an oil-quench.

**Rating the Machinability of Bullet Core Steel.** N. G. Meagley. (Metal Progress, 1943, vol. 44, July, pp. 67-71). The author discusses a modification of E. J. Janitzky's machinability index which takes into account the tensile strength and reduction of area in cold-drawing, and explains its application to the relatively hard steels for the cores of armour-piercing bullets. Janitzky's index has been explained previously (*see Journ. I. and S.I.*, 1939, No. I., p. 288 A).

**A Survey of Electrical Sheet Steels for Power Plant and the Factors Affecting Their Magnetic Properties.** F. Brailsford. (*Journal of the Institution of Electrical Engineers*, 1943, vol. 90, Part II., Oct., pp. 307-322). After a short discussion of the history of the development of electrical sheet steels the limitations imposed upon designers of electrical plant are referred to. This is followed by a brief outline of the physical basis of magnetic properties and by a discussion of how internal strains, grain orientation and alloying affect the magnetic properties of electrical steel sheets.

**The Tensile Properties of Alloyed Ferrites.** C. E. Lacy and M. Gensamer. (*American Society for Metals*, Oct., 1943, Preprint No. 15). The results of a systematic study of the effects of alloying elements in solid solution on the strength and rate of strain-hardening of ferrites of substantially constant grain size, as revealed by true stress-strain curves, are reported. Thirty binary iron alloys were prepared using chromium, cobalt, vanadium, aluminium, nickel, molybdenum, tungsten, silicon, titanium and beryllium. In addition, eleven ternary and quaternary alloys were prepared to study the combined effects of some of the alloying elements. The strengthening effect of an alloying element as a function of its concentration can be represented by a single coefficient, and those of several elements in solution together are simply additive.

**How to Conserve Our Supplies of Cadmium.** K. G. Soderberg. (*Steel*, 1943, vol. 113, Oct. 11, pp. 202-204). The possibilities of using lead, zinc, silver, tin or black-oxide coatings in place of cadmium are discussed and some methods of reducing cadmium losses where cadmium is essential are pointed out. The cadmium in "drag-out losses" can be reduced by: (1) Withdrawing the articles slowly from the solution; (2) allowing them to drain thoroughly; and (3) immersing them in a drag-out tank from which the cadmium is subsequently recovered.

**The Rôle of Toolsteel in the War Effort.** S. C. Spalding. (*Metal Progress*, 1943, vol. 44, Sept., pp. 425-430). The successive steps taken in the United States to reduce the amounts of tungsten, vanadium, nickel and molybdenum in tool steels are outlined. The maximum amounts of these elements now permitted in tool-steels for various purposes are given together with recommendations on the design of tools with a view to preventing breakages.

**Screw Machine Steels as Alloy Steel Substitutes.** A. S. Jameson. (*Iron Age*, 1943, vol. 152, Sept. 16, pp. 52-58; Sept. 23, pp. 46-50). The author presents data on the properties, in the case-hardened and heat-treated states, of low-carbon and medium-carbon steels of free-machining quality and compares them with those of low-alloy steels.

**Comparative Effects of Boron and Manganese on some Properties of Heat Treated Steel.** G. F. Comstock. (*Iron Age*, 1943, vol. 152, Sept. 9, pp. 48-52). The author has previously compared the

properties of molybdenum steel with those of steel treated with alloys containing boron and titanium (*see Journ. I. and S.I.*, 1943, No. II., p. 200 A). In the present paper the latter steels are compared with manganese steels. Several tables and graphs of the properties of boron-treated manganese steels are presented. If a pearlitic manganese steel with a tensile strength in the 140,000–260,000 lb. per sq. in. range in the quenched and tempered condition is required, better ductility and impact strength will be obtained by treating a 1·15–1·25% manganese steel with boron than by using a 1·8% manganese steel without boron.

#### **Effect of Sixteen Alloying Elements on the Hardenability of Steel.**

I. R. Kramer, R. H. Hafner and S. L. Toleman. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1636 : Metals Technology, 1943, vol. 10, Sept.). The authors present the results of several series of hardenability tests, employing factors calculated from Jominy end-quench test results, to determine the effect of additions of arsenic, antimony, beryllium, cobalt, columbium, germanium, tellurium, tin, aluminium and titanium on the hardenability of steel. Additional tests were made to extend the range of composition of some of the elements studied by Grossmann, namely, copper, chromium, manganese, molybdenum, nickel and silicon. Beryllium, arsenic, antimony, tin and aluminium increased the hardenability, whilst cobalt, columbium, titanium and tellurium decreased it; germanium had no effect. The results obtained by Grossmann for nickel, chromium, molybdenum and copper were confirmed. The results obtained for manganese agree with those reported by W. Crafts and J. L. Lamont. Silicon had a greater effect than that reported by Grossmann.

#### **Special Addition Agents Conserve Critical Alloying Elements by Replacing Important Amounts of Nickel, Chromium and Molybdenum.**

R. B. Schenck. (Society of Automotive Engineers : Steel, 1943, vol. 113, Oct. 4, pp. 96–104, 130). Data obtained by the General Motors Corporation on the effect of boron on the properties of steel are presented and discussed. Most of the tests were made on steels with 0·20–0·50% of carbon, and manganese in the four ranges 0·70–1·00%, 1·00–1·30%, 1·35–1·65% and 1·60–1·90%. The tables and curves show the increase in hardness and tensile strength obtained after a given heat treatment by adding increasing amounts of boron-bearing compounds per ton of steel, but the amount of boron in the compound is not stated.

#### **16-2 Stainless Steel.** S. P. Watkins. (Metal Progress, 1943, vol. 44, July, pp. 99–103). The properties of a stainless steel containing about 16% of chromium, 2% of nickel and 0·25% max. of carbon are discussed. This steel has been adopted by the Air Ministry and is known as S-80 in the British Standards Institution specification. The nickel increases considerably the amount of austenite formed at elevated temperatures, but the structure is not wholly austenitic at above the critical range, some ferrite being

present. The maximum hardness on quenching is 300 Brinell. It has excellent corrosion-resisting properties. Recommendations for machining this steel are given.

**User Report No. 18 on Experience with NE (National Emergency)**

**Alloy Steels.** A. S. Jameson. (Steel, 1943, vol. 113, Aug. 30, pp. 66-72). Data on the properties, microstructure and heat treatment of low-alloy nickel-chromium-molybdenum N.E. steel 9437 which is used for bolts in place of the S.A.E. 3100, 4000 and 4100 series of steels are presented.

**User Report No. 19 on Experience with NE (National Emergency)**

**Alloy Steels.** E. J. Wellauer. (Steel, 1943, vol. 113, Sept. 6, pp. 106-112). Data on the properties of heat-treated low-alloy steels with compositions within the following limits : Carbon 0·47-0·57%, manganese 1·00-1·35%, chromium 0·50-0·70% and molybdenum 0·10-0·20% are presented. Some of the steels were sulphurised in attempts to improve the machinability, but this was not very successful. These steels, which have been used for many years for making heavy-duty gears up to 8 in. in dia., are now classified among the National Emergency steels.

**User Report No. 20 on Experience with NE (National Emergency)**

**Alloy Steels.** W. J. Pierce. (Steel, 1943, vol. 113, Sept. 20, pp. 120-121, 134-136). Particulars are given of the system adopted by the Glen L. Martin Co., Baltimore, when the National Emergency steels were introduced in place of the S.A.E. alloy steels previously used. Tables are presented giving the S.A.E. steels, the new steels which can be substituted for them, and the appropriate heat treatment.

**Alloy Steel Has Advantages in Rock Drilling.** C. G. Kemsley. (Engineering and Mining Journal, 1943, vol. 144, Aug., pp. 82-83). The author discusses the extension of the use of alloy steel for hollow drills in Canadian mines and describes the hardening procedure and equipment adopted.

**Diagnosis and Prevention of Failures in Colliery Wire Ropes.**

A. E. McClelland. (South Wales Institute of Engineers: Iron and Coal Trades Review, 1943, vol. 147, Nov. 5, pp. 707-708; Nov. 12, pp. 751-752). The main causes of breakage of colliery wire ropes are classified and the contributing conditions reviewed. Internal wear is seldom the cause of a rope breakage unless internal corrosion is also present to render the former deterioration progressive. If corrosion has been responsible for a breakage, the wires will show tension fractures at parts considerably reduced by corrosion. When a rope breaks as a result of any form of fatigue or corrosion fatigue, all the wires will not show fatigue fractures, but a proportion will show normal tension fractures ; hence it is necessary to examine the broken ends of all the wires.

**The Selection and Care of Wire Rope.** J. U. Hoffman. (Iron and Steel Engineer, 1943, vol. 20, Sept., pp. 48-52).

The author describes some of the different "lays" and constructions of wire

ropes and their applications in steelworks. Recommendations for regular inspection and lubrication of wire ropes and sheaves are made.

## METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 30 A-33 A)

**Surface Replicas Containing Dye for Use in the Light Microscope.** V. J. Schaefer. (*Metal Progress*, 1943, vol. 44, July, pp. 72-74). A technique for producing replicas of metal surfaces which enables the relative depths of adjacent regions to be seen at a glance is described. The replica is made of a transparent layer of polyvinyl formaldehyde resin in which a dye is dissolved. Since the under surface of the replica follows the configuration of the etched sample, while, as the solvent evaporates, the upper surface remains flat, the part of the replica covering a deeply etched region will contain more dye than that covering an adjacent shallower area, and this difference in thickness will produce marked variations in light transmission which can be observed or photographed in the light microscope. A completed replica can be prepared in less than 5 min.

**The Electron Microscope : Its Applications in Metallurgy.** V. K. Zworykin. (*American Institute of Mining and Metallurgical Engineers : Metal Industry*, 1943, vol. 63, Oct. 22, pp. 258-260; Oct. 29, pp. 279-281). The author explains the principles of the electron microscope and describes the RCA (Radio Corporation of America) electron microscope with which resolutions between 20 and 30 Å have been obtained. This instrument has great versatility, for, with the aid of a special specimen holder, stereomicrographs can be prepared, and again, if the standard projector coil is replaced by a special unit incorporating a secondary specimen chamber and a weak focusing lens, the instrument is at once converted into a high-precision electron diffraction camera.

**Metallography with the Electron Microscope.** C. S. Barrett. (*American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1637 : Metals Technology*, 1943, vol. 10, Sept.). The work done at the Carnegie Institute of Technology with an RCA (Radio Corporation of America) type B2 electron microscope is reported. Forty-five electron photographs of copper, monel metal, high-speed steel, pearlite and martensite at up to 20,000 diameters are reproduced, almost all of which were obtained from silica replicas deposited upon polystyrene and floated from the polystyrene in ethyl bromide. The best resolution obtained to date is 40 Å, which is 100 times that possible with the optical microscope. Resolution in metallographic applications is limited by the details that can be developed by etching and transferred to

a replica; two spots 150 Å apart can be definitely resolved by the polystyrene-silica method. From electron photographs of the finest pearlite that could be produced in eutectoid plain carbon steel it was found that the minimum interlamellar spacing that occurs with reasonable frequency is about 500 Å. The nature of the attack by etching solutions and the structure of slip lines are discussed in the light of evidence obtained by the electron microscope.

#### **Interpretation of Electron Micrographs of Silica Surface Replicas.**

R. D. Heidenreich. (*Journal of Applied Physics*, 1943, vol. 14, July, pp. 312-320). Experiments are described for investigating the interpretation of polystyrene-silica surface replicas used in electron microscope technique. A polished and etched specimen of stainless steel is employed to show that the light microscope and electron microscope pictures are strikingly similar with corresponding regions easily recognised. The great value of stereoscopic pictures for determining relative surface elevations is demonstrated with a comparison of the topography as shown by the light microscope with oblique illumination. Resolution is discussed and a method of quantitatively determining the practical limiting resolution of replicas is described.

**Some Applications of the High Resolving Power of the Electron Microscope.** H. Green and E. F. Fullam. (*Journal of Applied Physics*, 1943, vol. 14, July, pp. 332-340). The high resolving power attained with the electron microscope has extended the field of pigment microscopy to cover particles falling within the range of 0.20-0.004 microns. High resolving power also brings into view many particles that would otherwise be invisible, and shows definite shape in particles which with optical instruments appear simply as diffraction discs.

**The Examination of Metals by X-Rays.** H. S. Cerruty. (*Australian Institute of Metals*, 1943, vol. 43, July 7, pp. 21-24). The author explains how X-rays are used to examine the atomic structure of metals. The derivation of formulæ to calculate the wavelength of X-rays and the relation between the wavelength and the angle to which the rays are diffracted, and the spacing of the atoms in the crystal under examination is given. Brief details of the production of radiographs by gamma rays are presented.

**Note on Some Unusual Microstructures Observed in Mild and Medium-Carbon Steels.** T. H. Schofield. (*Iron and Steel Institute*, 1944, this Journal, Section I). Envelopes sometimes observed surrounding the pearlite areas in mild and medium-carbon steels have been shown to be due to the separation of ferrite from the austenite during cooling from temperatures between the lower and upper critical points. By very slow cooling from this critical temperature range, or by heating steels showing such envelopes below the lower critical point, diffusion takes place and no envelopes are visible.

**Orientation in Low-Carbon Deep-Drawing Steel.** J. K. Stanley. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1635 : Metals Technology, 1943, vol. 10, Sept.). The development of orientation when cold-rolling low-carbon deep-drawing steel was followed by a method of measuring the magnetic torque. A linear relationship was found between the degree of orientation and the logarithm of the ratio of the final to the initial thickness. When the steel strip was cold-rolled in either the as-received, or recrystallised, or normalised condition, this linear relationship existed in all three cases. The change in degree of orientation on recrystallisation of the cold-worked material was also studied. A maximum in the degree of preferred orientation was found in the region of 65-75% cold reduction when the strip was subsequently recrystallised at 600° and 850° C. Prolonged annealing (up to 50 hr.) at 600° C. did not result in any improvement, but prolonged annealing at 850° C. increased the degree of orientation. It is known that heating the strip above the critical range destroys the preferred orientation, but complete random orientation does not occur unless the steel has been cold-worked a minimum of 40%. The magnetic torque method does not add any new knowledge on the nature of orientations after hot-rolling, except to indicate that complex orientations are produced.

**A Metallographic Study of the Decomposition of Austenite in Manganese Steels.** J. V. Russell and F. T. McGuire. (American Society for Metals, Oct., 1943, Preprint No. 6). The beginning of the transformation to martensite has been determined for three series of steels containing carbon 0.50%, 0.80% and 1.0% respectively, with manganese increasing from 1% to 11%. End-quench hardenability test data are presented as well as the S-curves for three of the 0.5% carbon steels. Increasing the manganese shifts the S-curves for the beginning and end of the transformation to the right, but the influence is greater on the latter curve. No rapid intermediate transformation has been detected. The carbides formed by isothermal transformation have the crystal structure of  $\text{Fe}_3\text{C}$ .

**The Effect of Varying Amounts of Martensite upon the Isothermal Transformation of Austenite Remaining after Controlled Quenching.** H. J. Elmendorf. (American Society for Metals, Oct., 1943, Preprint No. 10). The transformation of austenite to martensite has been studied for four steels (with 0.64-0.91% of carbon) by metallographic examination. The microstructures obtained by controlled quenching were employed to determine the effect of different amounts of austenite and martensite on isothermal transformations at 600°, 700°, 800° and 900° F. The presence of martensite in an austenite matrix materially shortens the time for completing the transformation ; the greater the amount of martensite the shorter the time. This acceleration of the completion of transformation may be due to stresses imposed on the system by the

martensite during the quench. The steels higher in carbon transformed faster than those lower in carbon, probably because the stresses on the system were greater with the high-carbon martensite. Holding the steel in the quenching agent for as long as 1 hr. has no harmful effect on the mechanical properties of the steel, and longer tempering times reduce the tensile strength but have very little effect on the ductility.

**Martensite Reactions in Alloy Steels.** P. Payson and C. H. Savage. (American Society for Metals, Oct., 1943, Preprint No. 11). By applying the technique of A. B. Greninger and A. R. Troiano (*see Journ. I. and S.I.*, 1940, No. I., p. 50 A) to specimens of 0.50% carbon steels, the effects of manganese, silicon, nickel, chromium, molybdenum and tungsten on the temperature at which the austenite-martensite reaction starts was investigated. This temperature is referred to as the *Ms* point. Carbon has by far the greatest effect in depressing the *Ms* point; manganese, chromium and nickel follow in that order; silicon, molybdenum and tungsten have little effect. From the experimental data the following formula was developed for calculating the *Ms* point of low-alloy steels in terms of multiples of the contents of carbon and alloying elements :

$$Ms\ (^{\circ}\text{F.}) = 930 - 570C - 60\text{Mn} - 50\text{Cr} - 30\text{Ni} - 20\text{Mo} - 20\text{W}.$$

This is valid provided that the austenitising temperatures used are sufficiently high to permit solution of all the carbides in the steel. As the *Ms* point is very sensitive to the carbon content, the procedure can be applied to determine the depth of decarburisation, or carburisation, in steels. As an example, the measurement of decarburisation in a high-speed steel is given.

**Influence of Nickel, Molybdenum, Cobalt and Silicon on the Kinetics and Ar" Temperatures of the Austenite to Martensite Transformation in Steels.** H. H. Chiswick and A. B. Greninger. (American Society for Metals, Oct., 1943, Preprint No. 12). A study has been made of the individual effects of nickel, molybdenum, cobalt and silicon on the kinetics and the Ar" temperatures of the martensite transformation in steels. By examining micrographs and differentiating between tempered (black) and untempered (white) martensite, the quantitative effect of the above elements on the Ar" point was observed (this is the method of Greninger and Troiano, *see Journ. I. and S.I.*, 1940, No. I., p. 50 A). Nickel (up to 15%) lowered the Ar" point of a 0.45% carbon steel uniformly at a rate of about 19° C. for every 1% added. Molybdenum (up to 2%) did not alter the Ar" points of steels containing 0.50%, 0.80% or 1.00% of carbon. Up to 3.5% of silicon also had no effect. Additions of 3.4-7.6% of cobalt raised the Ar" point of a 1.12% carbon steel uniformly at a rate of about 19° C. for every 1%. The kinetics and the mechanism of the austenite-martensite transformation as described by Greninger and Troiano is not in any way altered by the presence of any of the above alloying elements.

## CORROSION OF IRON AND STEEL

(Continued from pp. 33 A-34 A)

**The Probability-Integral of the *t*-Function.** U. R. Evans. (Engineering, 1943, vol. 156, Oct. 8, p. 295). To ascertain whether improvement in the behaviour of a metal (*e.g.*, greater corrosion resistance) is obtained by some device or protective treatment it is usual to carry out two sets of tests, one employing the device and one without it. If all the values obtained from the first set are superior to those given by the second, the benefit becomes apparent, but, when the scatter is serious (as when measuring corrosion-fatigue life), the two sets of values will overlap and doubt will then arise whether the apparent superiority is genuine or not. In such cases it has long been customary to calculate the so-called *t*-function and to find from statistical tables the probability that such values of *t* could have been obtained, even if the device was without influence, so that all the values really belonged to a single big set. The available tables, which were constructed for biological purposes, are not well adapted to the needs of the engineer or chemist. To facilitate statistical testing, curves have been prepared in the Corrosion Research Section at Cambridge University and these are reproduced in this communication; they show at a glance the probability of obtaining different values of the *t*-function. The curves were plotted by R. S. Thornhill, mainly for use in corrosion-fatigue research, and they may well prove useful in many analogous engineering problems.

**The Use and Misuse of the Salt Spray Test as Applied to Electro-deposited Metallic Finishes.** C. H. Sample. (ASTM Bulletin, 1943, Aug., pp. 19-21). The salt-spray test cannot be recommended as a quality test for electro-negative coatings. When the conditions are properly standardised the test is frequently useful for evaluating the porosity of electrolytic coatings of the electropositive type. The time of exposure in salt-spray tests required to reveal a given degree of porosity varies with the combination of base metal and coating being tested, and it should be correlated with actual exposure tests. The time required for the first rust spots to appear is not as important as the appearance of the coating after a given time in the salt spray. Further standardisation of the A.S.T.M. Tentative Method B117-41T is recommended.

**The Service Behavior of Plated Steel Wire as Indicated by the Corrosion-Fatigue Test.** J. N. Kenyon. (Wire and Wire Products, 1943, vol. 18, Aug., pp. 449-450, 471). The results of corrosion-fatigue tests on uncoated and coated 0.66% carbon steel wire drawn to 0.037 in. in dia. are presented. The coatings tested were bronze and hot-dip zinc covered with copper. The wire was held by two bearing-metal guides to form an arc so that a 15-in.

length was immersed in distilled water, and it was revolved at 6000 r.p.m. for 15 sec. by an electric motor, thus subjecting it to equal stress reversals. The uncoated and the bronze-coated wires behaved almost identically, whilst that with the zinc plus copper coating survived a much greater number of stress reversals. The unplated wire retained some ductility after the test and could be bent round a  $\frac{1}{4}$ -in. rod. The zinc-plus-copper plated wire could be bent easily round an  $\frac{1}{8}$ -in. rod, whilst the bronze-plated wire could be broken in  $\frac{1}{2}$ -in. lengths with the fingers.

## ANALYSIS

**Microchemical Analysis.** E. C. Pigott. (Iron and Steel, 1943, vol. 17, Oct., pp. 2-8; Nov., pp. 140-144). In view of the interest and usefulness of the application of microchemical methods of analysis to iron and steel, the author presents abridged translations of the following papers: (1) The Applications of Micro-Chemistry to Metallurgical Studies, by C. Benedicks and R. Treje (*see Journ. I. and S.I.*, 1936, No. II., p. 45 A); (2) Some Applications of Micro-Analysis in the Testing of Metals and Alloys, by A. Leroy (*see Journ. I. and S.I.*, 1938, No. II., p. 44 A); and (3) The Micro-Analytical Investigation of Metals, by N. Niessner. Accurate and rapid processes, exploiting photo-electric colorimetry, for determining carbon, sulphur, phosphorus, manganese, chromium and molybdenum in iron and steel on a few milligrammes of sample are also described.

**Developments in Micro-Chemical Analysis.** E. J. Vaughan. (Nature, 1943, vol. 152, Nov. 13, pp. 555-556). A résumé is given of a symposium on micro-chemical analysis arranged by the Micro-Chemical Club, the Royal Institute of Chemistry and the Sheffield Metallurgical Association. Applications of micro-analytical methods to various types of organic and inorganic materials are described. The most recent advance relating to metallurgy is the development of a composite method for the determination of manganese, molybdenum, chromium and nickel on a single 4-mg. sample. This has been achieved by the use of monochromatic light with a mercury lamp as light source together with suitable filters in the absorptiometer and the provision of special micro-cells containing as little as 0.5 c.c., but nevertheless permitting the passage of a narrow beam of light through a long column.

**The Nessler Reaction and Its Use in the Determination of Nitrogen in Commercial Ferrous Alloys.** A. Gotta and H. Seehof. (Iron and Steel Institute, 1943, Translation Series, No. 162). This is an English translation of a paper which was published in Zeitschrift für analytische Chemie, 1942, vol. 124, pp. 216-226. In preliminary

experiments the conditions to be chosen for accurate colorimetric determinations of nitrogen, using Nessler's reagent, were established. Based on the results of these experiments, a method for determining the nitrogen content of ferrous alloys was developed. In this method the solution of the sample obtained with sulphuric acid, or by decomposing with bisulphate and taking up the melt in water, is made alkaline with sodium hydroxide. The hydroxides precipitated are filtered off and an aliquot part of the filtrate examined colorimetrically. The main advantage of the new method is the saving in time due to the fact that the distillation of ammonia, inherent in all previous methods, can be dispensed with.

**Vacuum Fusion Analysis of Silicon Steels.** G. Derge and T. T. Omori. (Blast Furnace and Steel Plant, 1943, vol. 31, Aug., pp. 888-889, 913). The authors discuss the results of experiments designed to determine whether appreciable amounts of silicon in steel affect the results of oxygen determinations made by the vacuum-fusion method, for Zapffe and Sims have suggested that, in silicon steels, appreciable amounts of oxygen may be dissolved in liquid iron as silicon monoxide which is not readily reduced by carbon; the oxygen also cannot be extracted from the melt as carbon monoxide during the vacuum-fusion analysis. The results demonstrated that vacuum-fusion analyses are valid in the presence of at least 2·5% of silicon and there was no indication that this is the upper limit. The maximum permissible amount of silicon is probably that at which it combines with the carbon of the crucible to form silicon carbide, thus causing the crucible to fail.

**Gravimetric Determination of Tin in Steel (Other than Chrome Steel).** W. C. G. Wheeler. (Analyst, 1943, vol. 68, Aug., p. 246). A simple gravimetric method of determining tin in steels not containing chromium is described. The sample is dissolved in sulphuric acid and, after treatment with solutions, particulars of which are given, the tin is precipitated as stannic sulphide. This is ignited and the tin content is calculated from the weight of the residual oxide.

**The Determination of Sulphur and Phosphorus in Pig Iron.** (Iron and Steel Institute, 1944, this Journal, Section I). An account is given of the work of the Blast-Furnace Materials Analysis Sub-Committee of the Blast-Furnace Committee (a Committee of the Iron and Steel Industrial Research Council) on the determination of sulphur and phosphorus in pig iron, and details are put forward of methods recommended for accurate work. Suggestions are made as to the most appropriate methods of sampling iron, whether in the form of pigs or in the molten state. The combustion method for sulphur determination is described in detail and the work of members of the Sub-Committee in the development and standardisation of the method is set out. The work reported on the estimation of phosphorus in pig iron includes a study of the possible effects of arsenic and titanium on the results.

**A Briquetting Press and Electrode Loader for Spectrochemical Analysis.** H. C. Harrison and C. C. Ralph. (*Industrial and Engineering Chemistry, Analytical Edition*, 1944, vol. 15, July 15, pp. 466-467). An inexpensive and easily constructed apparatus is described for briquetting a powdered sample for spectrographic analysis, and for loading the briquette into an electrode crater without subsequent manual handling.

**Spectrographic Analysis of Alloy Steel.** P. R. Irish. (*Steel*, 1943, vol. 113, Aug. 9, pp. 100-105, 127-130). The spectrographical laboratory which has been in operation for over a year at the works of The Bethlehem Steel Co. is described. Over 5000 determinations are made each week, and these are used to control the production of alloy steels in fifteen furnaces.

**A Review of Spectrographic Analysis of Some Metals and Alloys.** J. Sherman and J. W. Jenkins. (*Journal of the American Society of Naval Engineers*, 1943, vol. 55, May, pp. 189-312; Aug., pp. 404-469). The authors present a comprehensive review of the factors involved in routine spectrographic analysis, discussing only such elementary theory and technical considerations as are necessary for clarification.

**Development in the Method for the Rapid Determination of Carbon and Hydrogen in Coal.** G. F. Fenton. (*Journal of the Society of Chemical Industry*, 1943, vol. 62, Oct., pp. 160-163). The combustion method for the determination of carbon and hydrogen in coals was modified so that, by using 250-300 c.c. of oxygen per min., combustion was completed in about 10 min., although the furnace was operated at the usual temperature of only 800° C. Magnesium perchlorate and soda-asbestos were used in the absorption train. This modification has been successfully applied in five different laboratories.

**An Analysis of English Fluorspars and Their Associated Minerals.** G. H. Osborn. (*Metallurgia*, 1943, vol. 28, Oct., pp. 261-264). The increasing use of home-mined fluorspars for metallurgical purposes has imposed a strain on English mines, and, as only a few mines have flotation and washing plants, the material is often heavily contaminated with associated minerals, thus making the task of analysis very difficult. In this paper a scheme of analysis is presented for the determination of the minerals likely to be found.

## REFRACTORY MATERIALS

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(Continued from pp. 39 A-40 A)

**The Drying of Magnesite Bricks. Part II.** J. H. Chesters and T. W. Howie. (*Transactions of the British Ceramic Society*, 1943, vol. 42, Oct., pp. 199-208). An apparatus is described for measuring the hydration-expansion of magnesite, and results are presented which show that it can be used to indicate the behaviour of magnesite batches on drying in brick manufacture. The results obtained with this apparatus confirm that the rate of hydration of magnesite increases rapidly with the temperature of drying, so that magnesite bricks should be dried at a low temperature with a high air velocity. The presence of dolomite, either freshly calcined or partially hydrated, or of caustic magnesite in a dead-burned magnesite may be expected to lead to trouble in drying bricks made from such a material. Autoclave treatment yields a product which is still reactive, and it is suggested that a less severe treatment, e.g., souring on a hot floor, is more suitable for dead-burned magnesites containing a proportion of calcined dolomite.

**Furnace Gas Pressure as Affecting the Life of Refractories.** S. M. Phelps. (*American Refractories Institute: Industrial Heating*, 1943, vol. 10, Sept., pp. 1352-1368). See *Journ. I. and S.I.*, 1943, No. II., p. 100 A.

**Monolithic Carbon Linings for Blast Furnaces. Part I.—Laboratory Investigations.** J. C. Hayman. (*Transactions of the British Ceramic Society*, 1943, vol. 42, Oct., pp. 185-198). The preparation of a coke-tar mixture is described, the data including a study of the effects of altering the charge-weight of coke fed to the pan mill. The present investigations were confined to a maximum grain size of 1 mm. From a consideration of workability, porosity, after-contraction, fired strength, and vaporisation of the volatile constituents of the tar, the optimum tar content for use in blast-furnace linings is thought to be about 10-11% by weight. On ignition at 600-900° C. in an atmosphere of town gas, such material became quite as strong as a German-fired carbon block, due to intense bonding by the residue from the tar. The permanent shrinkage after such ignition to 900° C. is only about 0.3%, and is of this order even after 60 hr. at 800-850° C. At 1450° C., however, it has been observed that the total permanent shrinkage is about 1%, which would cause some shrinkage at the hot face; this could doubtless be suitably dispersed by ramming the lining in panels such that a number of radial cleavages would be formed; lateral expansion between lining and shell is best allowed for by leaving a 4-in. space against the shell, which space is subsequently filled with a very lightly rammed coke-tar mixture.

In the green condition an unsupported specimen subsided quite rapidly under a load of 15 lb. per sq. in. at 100° C., but this would be of importance only in the event of the material being used as a foundation for the shell. After ignition to 900° C. the total porosity of rammed blocks was found to be lower than that of a German-fired block, whilst the refractoriness-under-load was above 1650° C. In the actual hearth the porosity after ignition was in some cases much lower than that of the German block. The heating up of the tarred material after ramming was studied having regard to the possibility of bursting taking place due to too rapid vaporisation of the tar during blowing-in, but mathematical and experimental work has indicated that there is no danger of this if a protective layer of firebrick 9 in. thick is put in.

**Measurement of the Thermal Conductivity of Fire-Clay Refractories.** T. C. Patton and C. L. Norton, jun. (*Journal of the American Ceramic Society*, 1943, vol. 26, Oct., pp. 350-358). A procedure has been described for testing dense refractories having thermal conductivities up to 15 B.Th.U. per hr. per sq. ft. per °F. per in. of thickness. The heat flow was measured by the method previously described by C. L. Norton, jun. (*See Journ. I. and S.I.*, 1943, No I., p. 73 A). The results obtained by different arrangements of samples and heating elements are shown. Further work will be necessary to determine whether this procedure will be satisfactory for materials, such as silicon carbide, having higher thermal conductivities than the above value.

**Spherical Furnace Calorimeter for Direct Measurement of Specific Heat and Thermal Conductivity.** J. R. Winckler. (*Journal of the American Ceramic Society*, 1943, vol. 26, Oct., pp. 339-349). A spherical calorimeter was constructed for measuring true specific heat and thermal conductivity. It was formed of two concentric spherical platinum shells, and a spherical sample was fitted into the inner shell. Heat was supplied electrically at the centre of the sample and the calorimeter was housed in a spherical electric furnace. The thermal conductivity was measured by determining the temperatures of the inside and outside of the sample at steady heat flow using the equation for heat conduction in a sphere. Specific heats and thermal conductivities were determined over the 100-2200° F. range for quartz sand, a chrome refractory cement, four types of insulating brick and an insulating material containing 85% of magnesia.

## FUEL

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(Continued from pp. 40 A-42 A)

**The Calorific Value and Specific Gravity of Coal.** (*Engineering*, 1943, vol. 156, Dec. 17, p. 484). A simple method of determining the specific gravity of coal from a  $\frac{1}{2}$ -lb. sample is described, and it is

shown how to obtain from this an approximate figure for the calorific value. As a basis it is assumed that the average calorific value of ash-free and moisture-free bituminous coal is 14,500 B.Th.U. per lb., that the specific gravity of pure bituminous coal substance is 1.2 and that that of pure ash substance is 2.5. It is suggested that the calorific value of ordinary bituminous coal is equal to 27,884–11,154 times the specific gravity. Careful laboratory tests on 31 samples of coal of widely varying quality showed, however, that there was no very definite relationship between the calorific values and specific gravities.

**Some Small Coal Jigs for Mechanical Cleaning of Coal at Truck Mines and other Low-Tonnage Operations.** B. W. Gandrud and G. T. Bator. (United States Bureau of Mines, Aug., 1943, Report of Investigations No. 3718). Descriptions are given of several types of coal-washing jigs with a capacity of 5–10 tons per hr. which are used in the Alabama coal fields.

**Byproduct Coke-Oven Tests of Washington Coals.** H. F. Yancey, J. Daniels, E. R. McMillan and M. R. Geer. (United States Bureau of Mines, Aug., 1943, Report of Investigations No. 3717). Investigations are described the object of which was to explore the possibilities of installing a Curran-Knowles by-product coking plant in the Puget Sound area of Washington to utilise Roslyn, McKay and Wilkeson coals alone, in combination, or mixed with petroleum carbon or petroleum coke.

**A Carbonization Pressure Gauge.** M. A. Mayers and J. A. Thompson. (American Institute of Mining and Metallurgical Engineers, 1943, Technical Publication No. 1631). A description is given of a gauge designed to measure the pressure exerted by the charge in a coke-oven on the oven wall. The gauge head consisted of bellows made of two thin cold-rolled steel sheets spot-welded together at their outside edges. The outer sheet was spot-welded to a cover plate against which the swelling coal exerted a pressure; the inner sheet was welded to the body of the instrument. Electrical contacts were provided inside between the faces of the bellows. Nitrogen was fed to the inside of the bellows to balance the pressure exerted by the charge. An increase in the nitrogen pressure separated the contacts and an automatic device operated a valve to reduce the nitrogen pressure until the contacts closed again. The pressure on the wall was determined from the nitrogen pressure, and temperature changes were recorded by means of a thermocouple inside the head. Even at high temperatures the life of the gauge-head was considerably greater than the coking time in full-scale plant.

**Effects of Acids and Alkalies upon Carbonization Products of Coal.** R. E. Brewer. (United States Bureau of Mines, Sept., 1943, Report of Investigations No. 3726). A review is presented of the literature on the effects of acids and alkalies—when used in various concentrations either in aqueous solution or in the dry state, at

different temperatures and pressures, and in the presence or absence of air—on the carbonisation products of different kinds of coal.

## FOUNDRY PRACTICE

(Continued from pp. 44 A-45 A)

**High-Grade Cast Iron from Low Pig-Iron Cupola Charges.** J. E. Rehder. (Foundry Trade Journal, 1943, vol. 71, Dec. 2, pp. 267-271, 274). The foundry practice at Walker Metal Products, Walkerville, Ontario, is described. High-grade castings for motor vehicles are now being made from low-grade raw materials, the cupola charge containing high proportions of steel flashings from a local forge and briquetted cast-iron borings. There is considerable variation occasionally in the composition and chill depth of the iron due to the character of the steel used. The principle followed to maintain close control is to bring the iron down the cupola spout with the composition essentially correct and with the subsequent chill too deep, and then to add an inoculant at the spout to adjust the chill depth and "modify" the iron. After tests over two years, the use of four inoculants has been made standard practice; these are artificial graphite, 80% ferro-silicon, high-carbon ferro-chromium and *SMZ* alloy (an alloy containing 60% of silicon and 6.0% of manganese). Additions other than graphite are made to the iron by slowly pouring them from a small can on a long handle on to the surface of the stream of iron as it flows over the lip of the cupola spout. The bottom of the ladle must be covered with iron before the addition is started, and the addition is completed when the ladle is two-thirds or three-quarters full. Graphite is added to the bottom of the ladle a few seconds before the iron is tapped into it. The five factors necessary for the effective use of inoculants, in order of importance, are : (1) Hot base metal, at 1480° C. at least, at the spout; (2) suitable base metal; (3) the inoculant to be selected by experience to give the desired properties in the casting; (4) the additions to be made in the proper manner; and (5) the iron to be used within 15 min. of the time of inoculation.

**Quenching Rate Versus Graphite Formation in Prequenched White Cast Iron.** O. W. Simmons. (American Society for Metals, Oct., 1943, Preprint No. 29). It has long been known that white cast iron will graphitise much more readily in the malleabilising treatment if it has been previously quenched from above the critical range. A report is presented of the effect of the rate of pre-quenching on the subsequent graphitisation of an iron containing total carbon 2.50%, silicon 1.30%, manganese 0.45%, phosphorus 0.082% and chromium 0.018% max. When the iron was pre-quenched from 1300° F. at a rate exceeding 240° F. per sec. to give

a hardness of Rockwell C 27 or greater, subsequent malleablising at 1680° F. resulted in very numerous and very fine graphite nodules which outlined the interdendritic cementite areas. Slower quenching rates to lower hardness values yielded progressively fewer and coarser graphite nodules on malleablising. The number of graphite nuclei formed appears to determine the rate of the subsequent graphitisation by its effect on the surface area available for the deposition of carbon arising from the dissociation of the dissolved carbide.

**The Mass Production of a Manganese Steel Casting.** J. W. Gardom. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Sept., pp. 86-132). A comprehensive account is given of the equipment, layout, difficulties encountered and procedure finally adopted at an English foundry for the mass production of cast manganese steel tank track links. The duplex melting process with three cupolas and two side-blown converters was used to produce the steel, and the ferro-manganese was prepared in a 33-in.-dia. cupola. Production eventually reached 550-600 tons of finished castings per month working one shift per day.

**Charts Data on Mold and Core Surface Behaviour at Pouring Temperatures.** H. W. Dietert. (*American Foundrymen*, 1943, Oct., pp. 2-5). A series of charts is presented in which the causes and remedies of defects in castings associated with the mould and core sand are conveniently tabulated.

**Correlated Abstract of Literature on Flowability and Deformation of Sands.** P. E. Kyle and F. R. Evans. (*American Foundryman*, 1943, vol. 5, Jan., pp. 4-8). A critical review of the literature on methods of measuring the flowability of moulding sands and their resistance to deformation is presented.

**Core Sand Reclamation at Elevated Temperatures.** D. L. Longeuville and O. J. Myers. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Sept., pp. 198-206). A brief account is given of the core-sand reclamation process at the works of the Wright Aeronautical Corporation. The principal item of the equipment is a long, slightly inclined, rotary kiln through which the used sand passes; at the discharge end of this kiln it is heated to slightly below the fusion point of silica, and this burns out the binding materials. Tests on new and reclaimed sand mixtures, each with the same amount of binder, showed that the reclaimed sand had lower tensile and transverse strengths, lower permeability and higher green compression strength.

**Thermal Process of Core-Sand Reclamation.** W. L. Hartley. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Sept., pp. 207-209). Additional data are presented on the rotary kiln method of reclaiming used core sand which is referred to in the preceding abstract. If only oil binders are used in the original mix, a very clean sand is obtained by the kiln process; when clay binders are used, some dehydrated clay particles adhere

to the sand grains after the kiln process. A kiln core-sand reclamation plant is considered to be an economic proposition for steel foundries producing 40–50 tons of castings per day and for grey iron foundries producing 50–60 tons per day.

**Constructing Boxes for Blowing Cores.** R. F. Lincoln and E. J. Swink. (*Foundry*, 1943, vol. 71, Oct., pp. 106–107, 202–205). The step-by-step processes in the making of aluminium boxes for blowing sand-cores for aero-engine cylinder-head castings are described.

**Stern Frames Cast in Cores.** P. Dwyer. (*Foundry*, 1943, vol. 71, Oct., pp. 99–101, 192). The method developed by the Penn Steel Castings Co., Chester, Pennsylvania, for preparing the moulds for casting steel stern frames weighing 15 tons is described. A complete pattern for the stern frame is made and its dimensional accuracy checked. It is then sawn in sections and each section is mounted in the bottom of a core box of substantial construction. Each box is placed under a sandslinger, packed with sand, moved a short distance, turned over and lifted, leaving a block of sand with the required impression. The blocks are dried in an oven and assembled on the floor of a concrete-lined pit to form a complete mould.

**Salving Porous Castings.** (*Iron and Steel*, 1943, vol. 17, Nov., pp. 145–146). Some particulars are given of a synthetic resin varnish and the method of applying it to seal porous castings. The defective casting is heated to about 300° F., held at this temperature for 30 min. and immersed in a tank of the varnish, in which it is allowed to cool. After removal of surplus varnish with a cleaning solvent, the casting is stoved for 30 min. to 1 hr. at 300° F. It is claimed that this treatment will effectively reclaim about 85% of all porous castings.

## PRODUCTION OF STEEL

(Continued from pp. 45 A–50 A)

**Brazil will Make Steel in a Brazilian Plant from Brazilian Minerals.** C. Longenecker. (*Blast Furnace and Steel Plant*, 1943, vol. 31, Oct., pp. 1129–1140). A report is presented of the progress made by the Companhia Siderurgica Nacional of Brazil in the construction of the integrated iron and steel works at Volta Redonda about 90 miles north of Rio de Janeiro. Particulars are also given of the location and nature of the ore, coal and limestone which will be supplied to the works. Completion of the plant is not expected until 1945, but some units are expected to be in operation in 1944.

**Iron and Steel Developments in Latin America.** (*Iron and Coal Trades Review*, 1943, vol. 147, Dec. 17, pp. 943–944). A brief

review of the economic position of the iron and steel trade of South America is presented. The difficulty of importing iron and steel from the United States and Europe has encouraged the erection of producing plant. Some particulars of the Volta Redonda plant in Brazil are given (*see p. 79 A*). Construction of a rolling-mill in Medellin, Colombia, which will have a capacity of 100 tons per day, is near completion.

**Improvements in the Layout of Modern Steelworks.** A. G. Arend. (*British Steelmaker*, 1943, vol. 9, Dec., pp. 542-545). Improvements in individual equipment and in the layout of steel-works plant are reviewed. These relate chiefly to the development of tilting open-hearth furnaces up to 120 tons, automatic gas and air reversing valves, the use of active and inactive mixers, and stripping equipment for the ingot moulds.

**Modern Weight Control in Steel Mills.** (*Steel*, 1943, vol. 113, Oct. 25, pp. 92-94, 119). Some examples of the use of modern weighing machines in steelworks are described and illustrated. Particular reference is made to the advantages of machines which make a printed record on either a strip of paper or individual tickets, and to machines for ore, coke, limestone, &c., which can be preset to weigh off batches of equal amounts; the latter incorporate mechanism which automatically cuts off the feed when the bin on the machine has been filled up to the required weight.

**Steel Melting Processes. I.—Huntsman.** (*British Steelmaker*, 1943, vol. 9, Dec., pp. 536-540). An account is given of the probable course of Huntsman's experiments in steel-making about 1742. The Huntsman process of steel-making was a small-scale one. The lasting merit of the crucible furnace is that it taught its operators the importance and control of casting temperatures, and the conditions under which almost perfect ingots could be made.

**The Study of the Thermal Performance of Open-Hearth Furnaces by the Correlation of Operating Data.** A. H. Leckie. (*Iron and Steel Institute*, 1944, this Journal, Section I). A method is outlined for investigating the performance of open-hearth furnaces by the statistical examination of routine works records (provided that these include the measurement of the fuel gas). In Section I, it is shown how the appropriate correlation methods may be used to determine the optimum gas rate and air/gas ratio, and to investigate the effect of many variables in a quantitative way and the changes in thermal efficiency under various conditions. The methods are illustrated by examples taken from actual practice. Section II, is devoted to the discussion of simple methods of measuring and calculating the quantities involved.

**Electric Furnace Operators Examine Operational Problems.** (*Iron Age*, 1943, vol. 152, Oct. 21, pp. 50-51, 136A-136D). This is a brief report on the first conference of the Electric Furnace Steel Committee of the Iron and Steel Division of the American

Institute of Mining and Metallurgical Engineers, held at Pittsburgh on October 1 and 2, 1943.

**Energy Conservation in Electric Furnaces.** A. G. Robiette. (*Journal of the Institute of Fuel*, 1943, vol. 17, Dec., pp. 31-33). Some factors affecting the operation of electric furnaces so as to obtain maximum efficiency are explained. Heat-treatment furnaces should be heated up during off-peak load periods and, where several furnaces are in operation, their heating-up periods should be staggered. When charging three-phase direct-arc furnaces, heavy scrap should be placed low down in the charge, the interstices being filled up with smaller or medium scrap. The superimposed scrap, if possible, should be selected so as to form as compact a mass as possible and one having a high resistance. Swarf should be packed on top of the charge, or kept for subsequent feeding to a molten bath. Approximately 80-160 kW. per ton per hr. are required to keep steel molten in a furnace; it is therefore imperative to hold metal in the furnace for the shortest possible period consistent with the steel-making practice adopted.

**Britain's Electric Furnaces for Melting and Heat Treatment.** E. N. Simons. (*Industrial Heating*, 1943, vol. 10, Sept., pp. 1259-1264). The development of electric metallurgical furnaces in Great Britain is reviewed. The Héroult furnace with three electrodes and the Greaves Etchell furnace in which the current, after arcing from the electrode to the metal, passes through the hearth to a copper plate attached to the hearth casing, are the types most frequently used for steelmaking. The tendency is to increase the melting voltages so as to obtain a faster melting rate and a lower current consumption per ton of steel.

**Rimming Steel.—An Examination of the Carbon and Oxygen Relationship in the Solidification of Basic Open-Hearth Steel.** T. Swinden, W. W. Stevenson and G. E. Speight. (*Iron and Steel Institute*, 1944, this Journal, Section I). Recent papers to The Iron and Steel Institute on the examination of rimming steels are discussed in the light of the "balanced" composition hypothesis of Hultgren and Phragmén. Comments are made on the effects of manganese and pressure on the value of the balanced composition, and it is suggested that, owing to the effects of pressure, a single balanced composition does not exist for all parts of the same freezing ingot. Experimental work consisted of the sampling and examination of five casts of rimming steel, in the range of pit-sample carbon analyses 0·04-0·14%. Calculated from the carbon and oxygen contents of the carefully prepared pit samples, the product (O)  $\times$  (C) is in close agreement with previously accepted values, and its significance in the five steels examined is discussed. Rolled sections of ingots, taken from the middle of the ingot position, were examined for their carbon and oxygen contents, determined in mid-rim and mid-core positions. A study is presented of the variations in these two elements in relation to the balanced composition as modified

by the presence of manganese and the effect of pressure. The results of the further examination of an ingot of rimming steel previously reported upon by Binnie (Journ. I. and S.I., 1942, No. II., p. 283 F) are given in an appendix. The oxygen and carbon values obtained in rim and core positions of top, middle and bottom sections provide additional interesting data on ingot position relative to the balanced composition.

## REHEATING FURNACES

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**The Design of Combustion Chambers in Forging Furnaces.** F. S. Bloom. (Industrial Heating, 1942, vol. 9, July, pp. 845-847). Curves are presented showing the rates of temperature increase at the surface and centre of various sizes of steel bars in a furnace held at 2250° F., and the conditions governing the rate of heat absorption of steel are discussed. Finally, data are presented relating the height of forging furnaces to the heat released per square foot of hearth area.

**Induction Heat is  $I^2R$ .** F. T. Chesnut. (Steel, 1943, vol. 113, Aug. 30, pp. 74-76). The theory of induction heating is explained and its application for heating bars for forging is discussed.

**Investigations and Proposals for the Better Control of Mill Furnaces.** F. Wesemann. (Iron and Steel Institute, 1943, Translation Series, No. 152). An English translation is presented of a paper which appeared in Stahl und Eisen, 1930, vol. 50, Nov. 13, pp. 1601-1610.

## ROLLING-MILL PRACTICE

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(Continued from p. 52 A)

**Standard Costs for Power Consumption of Rolling Mills.** F. Ryder. (Blast Furnace and Steel Plant, 1943, vol. 31, Sept., pp. 1030-1035; Oct., pp. 1152-1154). The calculation of power consumption in rolling mills was dealt with in an earlier paper (*see Journ. I. and S.I., 1943, No. II., p. 81 A*). In the present paper the mechanical and electrical losses involved in making the motor power available at the roll face are discussed. These losses include friction and the power consumed in starting, accelerating, reversing, decelerating and stopping.

**Formulæ for Hot-Rolling Steel.** E. Baumwald. (Australasian Engineer, 1943, vol. 43, Sept. 7, pp. 82-83). Formulæ for the energy consumed in rolling, the flow resistance and the rolling pressure applicable to the hot-rolling of steel are presented and discussed.

**Centralised Lubrication.** (Iron and Steel, 1943, vol. 17, Nov., pp. 157-158). A brief description is given of the Tanway system of lubrication for rolling-mill bearings. A Tanway installation comprises a central unit which forces lubricant through a main pipe-line to the point of application; a pressure monitor is installed in the pipe-line which automatically maintains the oil pressure in the line at a value directly proportional to the viscosity of the lubricant. The viscosity-pressure control operates whether the viscosity changes are due to temperature or to a change in the grade of lubricant.

**Effects of Temperature on Blooming Mill Production of Hot-Topped Steel.** H. J. Forsyth. (American Iron and Steel Institute : Iron and Steel, 1943, vol. 17, Nov., pp. 152-156). Some results of a study of the influence of ingot temperature on the efficiency of rolling operations and the surface quality of billets are presented and discussed. (See p. 16A.)

## PYROMETRY

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**Constant Heating Rate Control by the Thermocouple-Rectifier Bias Principle.** R. J. Smith. (Metal Progress, 1943, vol. 44, Oct., pp. 613-616). Some difficulties encountered in the design of apparatus for controlling the rate of temperature increase in electric furnaces are pointed out, and a detailed description is given of a method of controlling heating and cooling rates, which is based on the combined principles of the rectifier ammeter (for anticipation of power change) and the thermocouple (for initiating changes in the power supply to the furnace).

**The Emissivity of Molten Stainless Steels.** G. N. Goller. (American Society for Metals, Oct., 1943, Preprint No. 28). A study of the emissivity of molten stainless steels has been made by practically simultaneous thermocouple and optical pyrometer readings of heats melted in an experimental induction furnace. Emissivity values ranging from 0·40 to 0·75 were determined, depending on the analysis of the steel. The data are presented in the form of calibration charts for the optical pyrometer used for measuring molten steel temperatures in the casting pit. With increasing chromium, manganese, titanium or columbium, the emissivity increases; nickel, silicon, sulphur, or selenium plus phosphorus decrease the emissivity, whilst carbon and molybdenum have no appreciable effect.

**A Simple Temperature Control for Laboratory Electric Furnaces.** W. Hirst and C. G. Cannon. (Journal of Scientific Instruments, 1943, vol. 20, Aug., pp. 129-132). A description is given of an automatic furnace control, using a potentiometer bridge and a commercial photocell relay unit, which keeps the furnace tempera-

ture to within  $\pm 1^\circ$  C. when a chromel-alumel thermocouple is used, and also controls the run up to final temperature at any given uniform rate of heating within the limits of performance of the furnace winding. The apparatus can be constructed from standard components.

## HEAT TREATMENT

(Continued from pp. 53 A-56 A)

**Salt Baths—Their Use and Maintenance.** J. C. Newland. (Australian Institute of Metals: Australasian Engineer, 1943, vol. 43, Sept. 7, pp. 33-37, 53-67). The use of salt baths for hardening is reviewed. Some differences when using 50/50 cyanide/soda-ash mixtures and an accelerated cyanide bath are : (1) The former will give cases up to 0.030 in. deep and the latter up to 0.100 in. deep ; (2) cyanide/soda-ash mixtures are readily soluble in water, thus facilitating cleaning, whilst accelerated cyanides are not so soluble ; (3) cases made with the former mixtures are impregnated with nitrogen as well as carbon, and this tends to make them brittle ; (4) the former mixtures can be used for nitriding high-speed and austenitic steels ; and (5) the former mixtures have a tendency to fume at  $950^\circ$  C., whilst the latter are safe to use at this temperature. White-heart malleable cast iron can be case-hardened to depths up to 0.020 in. ; castings which have been well annealed can be carburised at up to  $900^\circ$  C., but the carburising time should be limited to 45 min. Scum on a cyanide bath should be removed as the crust forms ; it is also helpful to heat the salt to  $870^\circ$  C. for several hours and then return to the operating temperature. If the scum is very persistent, a handful of starch or cornflour thrown in will cause very rapid coagulation, and the scum can then be scooped off once and for all. The salt-bath heat-treatment of high-speed steel and of aluminium is also described, and recommendations on the cleaning of equipment are made.

**Carburizing Gears in the Electric Salt Bath Furnace.** W. F. Sorenson. (Metal Progress, 1943, vol. 43, Feb., pp. 237-240). An account is given of the carburising procedure for gears at a works manufacturing electrically driven vehicles and hoisting equipment. After experience with pack carburising and gas carburising, electric salt-bath furnaces heated by immersed electrodes have been found most satisfactory. The time required to produce a surface hardness of Rockwell C 58-C 62 and a case depth of 0.030 in. is about 3 hr. Cases produced in the salt bath have a slight and desirable degree of elasticity, whereas gas-carburised cases appear to have no elasticity whatever.

**The Action of Carbonate Catalysts in the Carburisation of Steel.** T. C. Fong and R. A. Ragatz. (American Society for Metals, Oct.,

1943, Preprint No. 17). An investigation of the effect of catalysts on the carburisation of steel was carried out in four parts. In Part I. the evolution of carbon dioxide from charcoal alone and from charcoal catalysed with sodium carbonate, barium carbonate and calcium carbonate at temperatures from 650° to 950° C. was studied. The curves relating the carburising time to the amount of carbon dioxide evolved all approach the horizontal after a preliminary heating time, the actual amount depending on the temperature and the catalyst employed. In Part II. the absorption of carbon dioxide by compounds catalysed with sodium hydroxide and barium hydroxide was examined. Whilst the hydroxides were rapidly converted into carbonates at relatively low temperatures, these carbonates were quickly decomposed on heating to temperatures in the range commonly used for carburising. In Parts III. and IV. two independent methods were employed to show that the catalytic action induced by the addition of sodium carbonate or barium carbonate is maintained even after evolution of carbon dioxide has attained a constant rate.

Sodium and barium carbonates are effective catalysts because : (a) They are able to react with carbon at temperatures below the minimum temperature for the direct dissociation into the metallic oxide and carbon dioxide ; and (b) the products of the reaction accelerate the rate of carburisation by increasing the carbon monoxide concentration and by speeding up the removal of carbon dioxide.

**Hardening High-Speed Taps and Dies in the Electric Salt Bath.** P. C. Farren. (Metal Progress, 1943, vol. 44, Oct., pp. 625-631). A detailed and illustrated description is given of the heat-treatment equipment and procedure for hardening screw-threading taps and dies at the works of the Greenfield Tap and Die Corporation. Side by side salt-bath furnaces heated by immersed electrodes are used. The preheating bath is kept at 1550° F. and the high-temperature bath at 2180° F. The tools are quenched in oil and the high-molybdenum steels are tempered at least twice at 1050° F. The heat-resisting electrodes for heating the baths contain no nickel, as this element plates out on the immersed tools ; the electrodes have an average life of 1200 hr. in the high-temperature bath.

**Control of Cyanide Hardening.** R. A. Chalmers. (Iron and Steel, 1943, vol. 17, Nov., p. 167). Methods of making analyses of cyanide hardening baths to determine the sodium cyanide, sodium carbonate, sodium cyanate, insoluble matter (plumbago) and moisture are briefly described.

**Thin Case Hardening.** V. W. Sherman. (Institute of Aeronautical Sciences : Heat Treating and Forging, 1943, vol. 29, Sept., pp. 452-455 ; Oct., pp. 533-535). The application of induction heating using frequencies in the 1-20 megacycle per sec. range for case-hardening to depths between 0.005 and 0.030 in. is discussed. The thickness of the surface layer in which the current is confined

varies inversely as the square root of the alternating current frequency. The problem of keeping the resistance high by means of a thin surface layer is of increased importance as the diameter of the work becomes smaller. The heat loss by radiation to the outside air is negligible as compared with the loss by conduction to the interior of the part being hardened, and electrical energy must be supplied from the induction heating unit at a rate at least double that at which heat is lost by conduction to the interior. By supplying electrical energy at a high rate, a 0.007-in. layer can be hardened to Rockwell C 60 without any heat-treatment effect on the core. This requires a frequency approaching 5 megacycles, a time of 0.6 sec. and an energy supply at three times the rate of loss by conduction.

**Heat Treating Output Doubled.** H. White. (Steel, 1943, vol. 113, Oct. 25, pp. 86, 117-118). An illustrated description is given of a unit for heat-treating bolts. It consists of an electrically heated furnace 22 ft. long, 6 ft. wide and 10 ft. high, through which a link conveyor belt slowly moves. At the discharge end the bolts fall down a covered chute into an oil tank, from which a sloping conveyor automatically lifts and discharges them into boxes. The furnace and chute to the oil tank are filled with a protective atmosphere made by partially burning natural gas. A high output of bolts with very uniform properties is obtained.

**Bright Gas Quenching of S.A.E. X-4130 and N.E. 8630 Welded Aircraft Tubes.** W. Lehrer. (American Society for Metals, Oct., 1943, Preprint No. 22). The development and advantages of a heat-treatment furnace for low-alloy welded steel tubes for aircraft are described. Much better physical properties were obtained by passing the tubes from the heating zone of the continuous furnace into a cooling zone, in which they were subjected to the blast of a large volume of cold gases issuing at high velocity from nozzles above and below the conveyor. Details of tests are given on steels S.A.E. X-4130 (carbon 0.30%, chromium 0.92%, molybdenum 0.18%) and N.E. 8630 (carbon 0.30%, chromium 0.50%, nickel 0.59%, molybdenum 0.20%). The cooling gas mixture used contained about 5% of carbon dioxide, 10% of carbon monoxide, 12% of hydrogen and a moisture content equivalent to a dew point of 40° F. The physical properties obtained in the steel were controlled by the rate of gas recirculation, the conveyor speed and temperature from which the tubes were cooled, and these had to be adjusted to suit the carbon content of the steel and the tube diameter and wall thickness. No cleaning or pickling of the heat-treated tubes was necessary.

**Wartime Applications of Industrial Gas Equipment.** E. G. de Coriolis. (American Gas Association : Metal Progress, 1943, vol. 44, Oct., pp. 647-648, 654-656). The main points of the author's paper entitled "Gas Fired Industrial Furnaces of the War and Post War Period" are republished in this article (*see Journ. I. and S.I.*, 1943, No. II., p. 157 A).

**High-Speed Heat Treatments.** F. O. Hess. (Steel, 1943, vol. 113, Nov. 8, pp. 114-116, 152-153). Some applications are described of the burners for flame-hardening which were referred to in a previous article (see Journ. I. and S.I., 1943, No. I., p. 86 A). These burn pre-mixed fuel-gas and air in specially shaped ceramic blocks. The applications include the hardening of caps for armour-piercing shell, tank track shoes and skate blades.

**Handling of Liquid Ammonia for Nitriding and Other Atmospheres.** C. V. Snell. (Metal Progress, 1943, vol. 43, Feb., pp. 245-248). As ammonia is being increasingly used in the heat treatment of steel, methods of storing it are of interest. In this paper data are presented on the storage capacity, fittings and methods of connecting up ammonia cylinders together with recommendations on safety precautions.

**Iron Alloy Scaling.** M. J. Day and G. V. Smith. (Industrial and Engineering Chemistry, Industrial Edition, 1943, vol. 35, Oct., pp. 1098-1103). An apparatus for making continuous weight-gain measurements of the scaling by air-oxidation of a large number of specimens simultaneously is described, and the results of 1000-hr. tests on 36 alloy steels at temperatures in the 1100-1700° C. range are presented. The results show that it is not safe to predict long-time scaling resistance from tests of only short duration. The steels investigated were alloyed with different amounts of chromium, molybdenum and silicon; of these, chromium contributes most to the scaling resistance when added in appreciable amounts, whilst for smaller additions, silicon is more effective.

**Measuring Decarburisation.** R. D. Chapman. (Metal Progress, 1943, vol. 44, Oct., p. 621). An example is given of the application of the Vickers micro-hardness-traverse method of measuring hardness to determine whether a molybdenum steel has been slightly decarburised during heat treatment.

**The Decarburisation of Cast Iron and Malleable Cast Iron in Hydrogen and in Mixtures of Hydrogen and Water Vapour.** W. Baukloh and A. K. Foroud. (Iron and Steel Institute, 1943, Translation Series, No. 165). This is an English translation of a paper which appeared in Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 355-362. See Journ. I. and S.I., 1943, No. II., p. 119 A.

**Hardening 35 Different Engine Parts on One Induction Machine at Cooper-Bessemer.** T. E. Eagan. (Industrial Heating, 1943, vol. 10, Sept., pp. 1282-1284). Brief particulars are given of an induction-hardening plant at the Cooper-Bessemer Corporation, Mount Vernon, Ohio, where a variety of Diesel engine parts ranging from  $\frac{7}{16}$ -in. bolts up to 6-in. dia. wrist pins are very rapidly heat-treated by using different fixtures and coils in one machine.

**Structural Changes during the Tempering of High Carbon Steel.** D. P. Antia, S. G. Fletcher and M. Cohen. (American Society for Metals, Oct., 1943, Preprint No. 31). The results of X-ray, metallo-

graphic, hardness, magnetic, dilatometric and specific volume studies of the mechanism of the tempering of a high-carbon steel, a very pure iron-carbon alloy (carbon 0.95%) and a 5%-nickel steel are reported. High carbon steel, whether of high purity or of commercial quality, passes through three pronounced stages during tempering. The first is the decomposition of the tetragonal martensite into an aggregate consisting of ferrite and a transition precipitate; this precipitate is not cementite, but ultimately transforms into cementite during the third stage. The second stage is characterised by the decomposition of the retained austenite into an acicular product having the same state of aggregation as the tempered martensite. The third stage is the genesis and development of cementite from the transition precipitate formed during the first two stages. Agglomeration of the cementite particles takes place during, as well as after, the third stage until a typical spheroidised structure is attained. All the tempering reactions are dependent on time and occur at lower temperatures with longer tempering times.

**The Effect of Carbon on the Tempering of Steel.** S. G. Fletcher and M. Cohen. (American Society for Metals, Oct., 1943, Preprint No. 32). The effects of the carbon content on the three stages in the mechanism of the tempering of steel were studied by means of magnetic, dilatometric, X-ray diffraction and hardness measurements. The three stages of tempering were described in an earlier paper (*see preceding abstract*). The work was confined to steels and high-purity iron-carbon alloys heat-treated so that only tetragonal martensite and retained austenite existed in the structure prior to tempering. The amount of retained austenite after hardening was determined by specific volume determinations and was found to increase rapidly with increasing carbon content. For a given carbon content the high-purity alloy retained less austenite than the commercial steel. All the steels tested exhibited the three stages of tempering previously reported, but in varying degree. The carbon appeared to have little effect on the temperature ranges in which these stages occur and on the rates of reaction within each stage. Extensive hardness test data indicated that the first stage (tempering of martensite) is a hardening reaction increasing in magnitude with increasing carbon content. While the decomposition of retained austenite (the second stage) is also a hardening transformation, the secondary hardening thus produced becomes pronounced only when more than 20% of austenite is initially present. The third stage (formation and growth of cementite) results in marked softening.

**The Tempering of Nickel and Nickel-Molybdenum Steels.** D. P. Antia and M. Cohen. (American Society for Metals, Oct., 1943, Preprint No. 33). Hardened plain carbon steels undergo the following three important phase changes on tempering: (a) decomposition of the tetragonal martensite into ferrite and a transition precipitate; (b) decomposition of the retained austenite into an

acicular structure; and (c) conversion into cementite of the transition precipitate formed during (a) and (b). The present paper reports an investigation of the effect of additions of 3·6% and 4·8% of nickel with and without molybdenum on these three stages of tempering of steels containing from 0·4% to 1·0% of carbon. Carbon and nickel promote the retention of austenite in hardened steel, but the carbon is much more effective. In these nickel steels, up to 0·5% of molybdenum causes a slight decrease in the amount of retained austenite. Nickel has a definite, but relatively slight, stabilising influence on the retained austenite during tempering. Carbon up to 1% and molybdenum up to 0·5% have very little effect on the stability of the retained austenite in these steels. The retained austenite decomposes either isothermally or on heating to the tempering temperature. There is no evidence of austenite decomposition on cooling from the tempering temperature, such as occurs with high-speed steel.

**Effect of Quenching-Bath Temperature on the Tempering of High-Speed Steel.** P. Gordon, M. Cohen and R. S. Rose. (American Society for Metals, Oct., 1943, Preprint No. 34). The relationship between the quenching bath temperature and the tempering characteristics of a high-speed steel containing tungsten 5·87%, chromium 4·07%, vanadium 1·50% and molybdenum 4·84% were studied by means of magnetic, dilatometric and hardness measurements. Single tempering for  $2\frac{1}{2}$  hr. at 1050° F. is sufficient to cause complete transformation of the retained austenite in this steel if the previous hardening quench is carried to room temperature, but, if the previous quench is to a point above room temperature, appreciable quantities of austenite remain in the steel after this single tempering. The transverse strength of the steel after arrested hardening and this tempering decreases considerably as the quenching bath temperature is raised. Raising the tempering temperature above 1050° F. decreases the amount of austenite retained after arrested quenching and simple tempering, but there is a large decrease in hardness. After arrested quenching, prolonged single tempering at 1050° F. does not cause the disappearance of all the austenite. Decomposition of all the austenite after arrested quenching can, however, be achieved in  $2\frac{1}{2}$  hr. at 1050° F. if double or multiple tempering is applied. A tentative explanation for the different effects of single and repeated quenching is presented. Repeated tempering causes a significant increase in the transverse strength of the steel. When the quenching bath temperature is appreciably above room temperature and double tempering is needed to decompose all the retained austenite, a third temper improves the strength properties still further.

## WELDING AND CUTTING

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(Continued from pp. 56 A-59 A)

**The Influence of Welding Defects on the Resistance to Fatigue of Welded Steel Joints.** J. Dearden. (*Transactions of the Institute of Welding*, 1943, vol. 6, July-Oct., pp. 120-122). A critical review of the literature on the influence of welding defects on the fatigue strength of welded joints is presented. The presence of defects reduces the endurance of welded joints to repeated loading, and failure under these conditions commences at one of them. Defects are not additive in their effect, and the removal of the most severe stress raiser from the joint increases the endurance only so far as the remaining stress raisers permit; if one of these is severe, little improvement in endurance will result. Condemnation of a butt weld because of relatively slight internal defects is not justified if the reinforcement has not been removed or if undercut is present. High endurance values are achieved only by the complete elimination of all the major stress raisers in a welded joint.

**Experiments with the Fabrication of an Aero Engine Exhaust Manifold in Austenitic Chromium-Nickel Steel.** K. J. B. Wolfe. (*Transactions of the Institute of Welding*, 1943, vol. 6, July-Oct., pp. 123-134). Experiments have been carried out to find suitable materials and welding technique for the mass production of a radial-type aero-engine exhaust manifold. It is shown that austenitic steel sheet materials recommended as "immune from weld decay" suffer intercrystalline corrosion in the Hatfield test after welding. (The Hatfield test consists of boiling the weld for 72 hr. in acidified copper sulphate solution after heating the test-piece to 650° C. for 30 min.). Oelsen cupping tests were made before and after this treatment for comparison. It is necessary to use a molybdenum-bearing 18/8 type of steel sheet, and an 18/8 electrode has been produced containing both molybdenum and columbium as stabilising agents. Welds produced with these materials do not suffer intercrystalline corrosion in the Hatfield test. The electrochemical potential differences between various materials in the sheet and weld-deposit form have been determined, and these results indicated why failure has occurred in some of the welds.

**Resistance Welding—No. 1: Processes and Machines.** K. Rose. (*Metals and Alloys*, 1943, vol. 18, Sept., pp. 518-524). Portable and pedestal machines for spot and seam resistance welding are described and illustrated, and details of some of the processes are given. In some cases stored-energy systems have been devised in which energy is drawn from the supply line between welds, stored in a transformer or in a bank of capacitors, and drawn off to supply the peak current when the welding circuit is closed; three-phase current is rectified to direct current for these storage types of

equipment, so that the procedure is sometimes called D.C. welding. Some typical spot-welding operations are described.

**Arc-Welded Die Sets.** I. V. Stovern. (*Iron Age*, 1943, vol. 152, Nov. 4, pp. 62-65). Examples are given of the application of electric welding to the making of die sets. For simple forms of die it has been found practicable to apply coatings with a self-hardening tool-steel electrode to wearing surfaces and edges; these require no heat treatment and need only grinding to size. Two crude hole punches for rough work were made by inlaying hard cutting edges on mild-steel shanks, and they proved very successful. A great saving in the quantity of tool steel required and in expensive machining operations is achieved.

**Ammonia Converter of Welded 5% Chromium Steel.** J. Schuyten. (*Metal Progress*, 1943, vol. 43, Feb., pp. 218-223). The advantages of making an ammonia converter of welded 5% chromium steel plate instead of by the seamless forging of carbon steel are outlined. The vessel in question was 45½ in. in outside dia., 23 ft. long and  $\frac{3}{4}$  in. thick. It was welded with 25/20 chromium-nickel steel electrodes. The sequence of the manufacturing processes is described, and it is shown that, from the point of view of purchase price, time of delivery and resistance to hydrogen attack the welded chromium steel vessel was greatly superior.

**Chain Cables.** T. Scott Glover. (*Institution of Engineers and Shipbuilders in Scotland: Engineering*, 1943, vol. 156, Dec. 10, pp. 477-480). A comprehensive account is given of the manufacture of stud link chain cables for ships. Several designs of link are illustrated and details of the electric welding machines for making the joints are given.

**The Repair of High-Speed Steel Tools by Welding and Brazing.** H. Thomasson. (*Transactions of the Canadian Institute of Mining and Metallurgy*, 1943, vol. 46, pp. 333-341). Descriptions are given of three methods of repairing tools. The first is the low-temperature silver-soldering of broken parts of high-speed steel cutting tools of relatively small cross-section. The second is the repair by welding of broken or worn non-cutting portions of tools such as shanks and tongs. The third is the building-up of worn or broken edges of tools using electrodes of molybdenum high-speed steel. A technique is described which enables the full length of welding electrodes to be used. For this, a permanent stub end  $\frac{5}{8}$  in. in dia.  $\times$  3 in. long is held in the jaws of the electrode holder, and the operator makes a light butt weld between the stub end and the top end of each electrode; when welding, the arc is broken as soon as this joint is reached.

**Flame Cutting Applications Greatly Expanded by Improvised Setups.** F. Waldo. (*Steel*, 1943, vol. 113, Oct. 18, pp. 82-83, 121-123). Some examples are given of time-saving applications of the oxy-acetylene cutting tool in steelworks. These include the cutting of stacks of thin plates all to one shape and the setting up of a

machine carrying eight burners to cut  $3\frac{1}{2}$ -in. steel plate into  $3\frac{1}{2}$ -in. square billets where no billet mill is available.

## MACHINING

**Stainless Steel.** (Automobile Engineer, 1943, vol. 33, Oct., pp. 419-420). Recommendations are made and data are presented for the rough-turning and finish-turning of austenitic chromium-nickel steels of up to 50 tons per sq. in. tensile strength.

**Mortar Shell.** G. E. Sears. (Steel, 1943, vol. 113, Oct. 25, pp. 74-75, 96-104; Nov. 1, pp. 92-98, 126-135). A detailed description is given of the sequence of machining operations in the mass production of 4·2-in. mortar shells from seamless steel tubing.

**Machinability Ratings of Metals and Cutting Fluid Recommendations.** O. W. Boston, H. L. Moir, W. H. Oldacre and E. M. Slaughter. (Metal Progress, 1943, vol. 44, Oct., pp. 622-624). Tables are presented giving the Brinell hardness and machinability ratings of a large number of steels to American Iron and Steel Institute Specifications and of some of the National Emergency steels. Another table lists ten machining operations in order of severity together with the cutting fluid recommended for each for ferrous and non-ferrous metals of different machinability ratings. Some general information on cutting fluid selection is also given.

**Duplex Test-Piece Miller.** (Iron and Steel, 1943, vol. 17, Nov., p. 144). A description is given of a milling machine with two heads for rapidly and accurately finishing rectangular test-pieces 18 in.  $\times$  3 in. with a parallel shank 9 in. long reduced to  $1\frac{1}{2}$ - $2\frac{1}{2}$  in. in width.

**Operating a Modern Salvage Department.** K. A. Fowler. (Metals and Alloys, 1943, vol. 18, Aug., pp. 282-286). The author outlines a scheme for the collection and sorting of salvage in engineering shops. Colour coding is a very convenient plan; with this, all trays and bins are given a distinctive colour mark and each class of metal scrap is assigned its own colour, so that each set of bins is used for only one material. The re-use of waste material from a particular process should be enquired into. Scrap from large stampings can frequently be used as raw material for smaller stampings. Cast-iron borings and crushed steel turnings can be briquetted and the briquettes used as heavy scrap in the cupola. Other salvage operations discussed include trichlorethylene recovery, oil purifying, and the hard chromium plating of tools to prolong their life.

## CLEANING AND PICKLING OF METALS

(Continued from pp. 20 A-21 A)

**Removing Scale and Sludge by Chemical Treatment.** L. W. Lee and E. C. Hardy. (Steel, 1943, vol. 113, Nov. 1, pp. 106, 120-122). The conditions for the successful removal of scale from heat exchangers are discussed. Motor-vehicle units carrying a tank of solvent solution and the requisite pumps, pipes and valves are now available for the rapid descaling of heat exchangers during periods when the plant is shut down.

**Flame-Conditioning Steel Mechanically.** I. H. Such. (Steel, 1943, vol. 113, Nov. 8, pp. 112, 150-151). A detailed description is given of the oxy-acetylene billet and slab-conditioning machine at the works of the Youngstown Sheet and Tube Co. The machine is placed on a table immediately adjacent to the blooming-mill run-out table. The machine comprises a carrier for moving and supplying four banks of twelve burners each, with a hood and fan for removing smoke and fumes, equipment for removing slag by gravity and water, and an elevated control booth. The burners are set slightly over 1 in. apart. The machine will condition square billets from  $3 \times 3$  in. to  $14 \times 14$  in. and rectangular slabs up to 14 in. wide. The depth of cut is based upon the speed of the machine and the pressure of the cutting oxygen; it is generally operated at from 80 to 125 ft. per min. with the oxygen at 40 to 60 lb. per sq. in.

**Metal Cleaning before Processing.** K. D. Kahn. (Iron Age, 1943, vol. 152, Sept. 9, pp. 62-65). The author briefly reviews a number of metal-cleaning processes. A quick process for cleaning steel is to wash the material with a mild alkaline solution pumped through nozzles; this is followed by a water rinse, and while the parts are still wet they are wiped with a cloth moistened in one of the proprietary cleaners containing both chromic and phosphoric acid. After drying, a good surface is left for a priming coat.

**Processing Layouts for Metal Cleaning.** C. W. Smith. (Machinist, 1943, vol. 87, Nov. 6, pp. 101-104; Dec. 4, pp. 97-98). Recommendations are made for the selection and layout of equipment for solvent degreasing, mechanical washing and alkali cleaning in tanks, and the following typical problems are discussed: (1) Cleaning steel for heat-treating operations; (2) cleaning iron, copper and aluminium alloys for annealing and drawing; (3) cleaning steel for selective carburising, nitriding and cyaniding; (4) cleaning aluminium alloys for anodising and prior to spot welding; (5) cleaning steel for painting and phosphate coatings; and (6) cleaning metals for electroplating.

**Industrial Metal Finishing. Part III.: Polishing Processes. Part IV.: Overcoming the Problems of Degreasing and Cleaning.** H. Silman. (Sheet Metal Industries, 1943, vol. 18, Sept., pp. 1567-

1574, 1602; Nov., pp. 1935-1940). Continuation of a series of articles (*see Journ. I. and S.I.*, 1943, No. II., p. 160 A). The polishing of metals in lathes and automatic machines, and different types of buffing wheels and abrasives are described in Part III. In Part IV. particulars are given of organic solvents, chlorinated hydrocarbons and stabilisers for solvents used in degreasing with descriptions of different types of degreasing equipment.

**Evaluation of Metal Cleaners.** H. Strow. (*Metals and Alloys*, 1943, vol. 18, Sept., pp. 503-505). It is shown that measurements of the pH value, emulsifying power, surface tension and buffering action are not satisfactory means of judging metal cleaning solutions. Morgan and Lankler have developed a test in which a standard form of stain is produced on test panels; the panels are cleaned and then photographed under special conditions which cause any unremoved oil to fluoresce. There is no recognised method of determining the life of a cleaning solution, but a method suitable in some cases is to foam the used solution and, if the volume of foam is half, or more than half, the original volume, then the solution has reached the end of its useful life.

**War-Time Disposal of Waste Pickle Liquors.** W. G. Imhoff. (*Wire and Wire Products*, 1943, vol. 18, July, pp. 389-392). The author describes a plant for the treatment of waste pickling liquor; this has been in continuous operation for about 25 years with practically no repairs. The method is referred to as the "basin system," for it consists of passing the liquor from one basin to another, treating with lime, filtering through crushed stone and sand, and finally emptying a clear, tasteless and harmless water into the nearby river. A diagram shows the layout of the settling, neutralising and sludge tanks and the filter beds.

**Recovery of Free Acid from Pickling Liquors.** H. W. Gehm. (*Industrial and Engineering Chemistry*, Industrial Edition, 1943, vol. 35, Sept., pp. 1003-1004). Experiments have been made to determine the relative effectiveness of several alcohols and ketones to promote the crystallisation of ferrous sulphate in waste pickling liquors. Acetone proved the most effective, being superior to the fatty alcohols such as methanol. Liquor from the batch process was best treated with an equal volume of acetone; this removed 85% of the ferrous sulphate and increased the acid concentration by 71%. For this process to operate economically, a high recovery of acetone would be necessary; in laboratory experiments 97% recovery was obtained in an open system. Large-scale closed-system operation of the acetone process should realise recoveries well in excess of 99%. The ferrous sulphate recovered in this manner is free from acid and in a relatively dry state.

## COATING OF METALS

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(Continued from pp. 21 A-25 A)

**Chemical Blackening Process for Steel Finds New Favour as Production Tool.** A. P. Hill. (*Steel*, 1943, vol. 113, Nov. 1, pp. 100, 136-139). A process of producing black matt surfaces on steel is described. After cleaning, the parts are dipped for about 10 min. in a solution, the principal ingredient of which is usually sodium hydroxide with small additions of potassium nitrate and sodium nitrate. The bath is kept at boiling point which is about 295-300° F.

**Cylinder and Ring Life with Porous Chromium-Plated Rings.** T. C. Jarrett. (*Mechanical Engineering*, 1943, vol. 65, Sept., pp. 633-635). The author gives details of a chromium-plating process which produces a porous coating. Such a surface has proved to be advantageous on the side face of piston rings because of its oil-retaining properties. The chromium is deposited, using a high current density, to form a coating 0·004-0·006 in. thick. The current is then reversed to produce a stripping action which results in a porous layer 0·001-0·0015 in. thick. Details are given of the hardness and wear of cast-iron piston rings plated in this manner after trials in aero-engines.

**Chromium Plate: Its Thickness and Finish Requirements.** T. G. Coyle. (*American Society for Testing Materials: Steel*, 1943, Sept. 6, pp. 118, 145-149). The author makes recommendations within the framework of the A.S.T.M. tentative specification B117-43T for the chromium-plating of steel for engineering purposes. The recommendations cover the finishing treatment for specific applications such as plug gauges, ring gauges, cutting tools and pump parts.

**Some Aspects of Metal Finishing.** H. Silman. (*Sheet Metal Industries Association: Sheet Metal Industries*, 1943, vol. 18, Oct., pp. 1781-1785; Nov., pp. 1945-1947). The author reviews metal-coating processes. A high degree of precleaning of the work is essential if good adhesion of the deposits is to be obtained and, for mass production, it is desirable to have a cycle of several cleaning operations to ensure a high standard of chemical cleanliness. The protective value of a polished nickel deposit is often better than that of a dull plate of equal thickness, but, as polishing removes some of the metal, it is advisable not to polish the nickel deposit when appearance is a secondary consideration. The protective value of chromium as a direct deposit is small, and it is generally applied in thicknesses of the order of 0·00001-0·00002 in. over a nickel deposit which should not be less than 0·001 in. thick.

Infra-red lamp installations for drying enamel coatings are becoming popular. In many of these the air temperature is very

low and no real attempt is made to conserve convection heat, so that, although the efficiency of the lamps may be high, that of the plants themselves is very low. This can be tested by measuring the energy given out by the lamps and comparing this with the calories absorbed by the work being treated.

**Zinc Plating from Sodium Zincate Solutions.** N. A. Tope. (*Journal of the Electrodepositors' Technical Society*, 1943, vol. 18, pp. 127-137). An account is given of the technique adopted at a plating works where grit-blasted steel surfaces, which were formerly cadmium-plated, had to be zinc-plated without the use of acid pretreatments. Details of experiments with a number of solutions are given. The solution eventually found to be most satisfactory was prepared by dissolving caustic soda in a minimum amount of water using 40 oz. of soda for every gallon of solution required; 37 oz. of zinc sulphate crystals per gallon were added to the boiling solution; when all the soluble salts were dissolved, 10 oz. of Rochelle salt per gallon were added. After cooling, the solution was treated with small quantities of solid carbon dioxide. After allowing it to stand, the supernatent liquor was syphoned off into the plating vat, and to this were added 6 oz. of sodium sulphate and 4 oz. of sodium cyanide, dissolved in hot water, per gallon of plating solution. After diluting and mixing, the solution was ready for use. In no case was zinc deposited on to a freshly grit-blasted steel surface unless the current density exceeded 15 amp. per sq. ft.

**Determination of Tin Coating Weights.** G. H. Bendix, W. C. Stammer and A. H. Carle. (*Industrial and Engineering Chemistry*, Analytical Edition, vol. 15, Aug., pp. 501-504). The authors describe a procedure for the electrolytic removal of tin from tinplate in the presence of potassium iodate and iodide. After removal of the coating the excess iodine is back-titrated with sodium thiosulphate and the weight of tin is calculated from the amount of potassium iodate consumed. The method is accurate and suitable for control laboratories of tinplate mills where several thousand determinations per week are made.

**The Testing of Continuity of Thin Tin Coatings on Steel.** R. Kerr. (*Engineering Inspection*, 1943, vol. 8, Autumn Issue, pp. 22-26, 31). Three tests for estimating the porosity of thin coatings of tin on electrolytic tinplate are described. The first is a modification of the hot-water porosity test as described by D. J. Macnaughtan S. G. Clarke and J. C. Prytherch (*see Journ. I. and S.I.*, 1932, No. I., p. 159), in which the immersion time is 40 min. at 95° C. The second is a modified ferricyanide paper test, and the third is one which does not reveal individual pores, but indicates the amount of iron exposed at the surface; in the third test the amount of iron dissolved from the specimen by exposure to an acid thiocyanate solution for a given time is determined colorimetrically.

**Electronics in Postwar Industry.** A. C. Montieth. (*Steel*, 1943, vol. 113, Nov. 1, pp. 109, 118). Many examples are given of

recent applications of electronics in the steel industry, in particular for the control of high-frequency currents used to heat electrolytically coated tinplate so as to melt the tin momentarily and thus fill up any porous areas. Some possible future applications are discussed.

**The Repair of Worn or Over-Machined Parts by Electrodeposition.** A. W. Hothersall. (Institution of Mechanical Engineers : Engineering, 1943, vol. 156, Nov. 26, pp. 438-440). Data are presented on the tensile properties and adhesion of copper and nickel electroplated deposits on steel, and electrodeposition as a means of building up worn or over-machined parts is discussed. A very strong smooth coating of nickel or chromium having little or no internal stress has little effect on, or may even increase, the fatigue strength of a steel of 40-50 tons per sq. in. tensile strength, while highly stressed and mechanically weak deposits of nickel may reduce the fatigue strength by as much as 50%. Chromium coatings generally appear to reduce the fatigue strength of steel less than nickel coatings. Chromium coatings are glass hard and can only be ground ; they are extremely brittle and the rate of deposition is less than that of nickel, especially on shielded or recessed surfaces.

**Iron Plating.** W. B. Stoddard, jun. (Electrochemical Society, Oct., 1943, Preprint No. 84-5). An improved chloride iron-plating solution is described ; it contains 200-500 g. per litre of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  plus 3-5 g. per litre of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . The temperature range over which this solution will produce heavy fine-grained ductile deposits is a broad one ( $70$ - $105^\circ\text{C}$ ). The physical properties of the plate are given.

**Novelties in Electroplating.** O. P. Watts. (Electrochemical Society, Oct., 1943, Preprint No. 84-9). Some experiments in the production of multi-coloured electroplates, the codeposition of nickel and copper and the deposition of chromium with either copper, nickel or iron are described. A brilliant multi-coloured plate was obtained with a solution of 20 g. per litre of ammonium molybdate with 1 g. per litre of sodium cyanide. The process is called "rainbow plating" from the banded arrangement of the colours. Several solutions with which nickel and copper were codeposited are described. Attempts made to deposit chromium together with copper, nickel or iron proved unsuccessful.

**Corrosion Resistance of Silver Plated Steel : Phosphating the Steel Plating.** P. J. Lo Presti. (Electrochemical Society, Oct., 1943, Preprint No. 84-3). Experiments are described in which samples of steel strip were phosphatised as a preliminary to plating with silver. Phosphatising was found to increase considerably the adhesion of the silver to the steel. It appears that although most, if not all, of the phosphate coat disappears during the first stages of silver plating, the phosphate coat protects the steel surface during that brief interval before the silver is discharged and deposited. Six photomicrographs are presented which support this conclusion.

**New Phosphate Coatings with Unusual Corrosion Resistance.** G. Jernstedt. (Electrochemical Society, Apr., 1943, Preprint No. 83-30). Methods of improving the corrosion resistance of phosphate coatings on galvanised steel are described. Chromate finishes were rejected because of their inherent film thinness and the breakdown of the film at temperatures below 100° C. By applying a special predip prior to phosphatising, the corrosion resistance of the resultant film can be appreciably improved, and metal parts with this finish do not always need a supplementary organic coating. The activity of the titanium disodium phosphate predip is probably due to the adsorption of a film containing the phosphate iron on the metal surface prior to the treatment in a phosphoric acid bath. The titanium is no doubt present in the predip as a colloid and possibly as a complex phosphate compound. Other compounds besides disodium phosphate can be used as a carrying medium. These are limited, however, and are not so effective as disodium phosphate.

**Metal Spraying by the Wire Process.** W. E. Ballard, G. F. Fairbairn and F. S. Pilkington. (Transactions of the Institute of Marine Engineers, 1942, vol. 54, pp. 1-6). After explaining the principles of the wire-spraying pistol, the authors discuss its development as a method of applying metal coatings. The aluminising process for protection against oxidation at elevated temperatures and the spraying of harder metals for building up worn parts are described, with information on the properties of such coatings. Several examples of the application of the process to specific problems in marine engineering are given.

**Metallizing.** N. C. Jones. (Chemistry and Industry, 1943, vol. 62, Dec. 18, pp. 481-482). A brief description is given of the process of metal spraying and the equipment used for it. Data are presented showing the weights of different metals which can be deposited per hour with two types of spraying pistol.

**Post-War Prospects and Developments in the Vitreous Enamelling Industry.** J. T. Gray. (Institute of Vitreous Enamellers : Foundry Trade Journal, 1943, vol. 71, Oct. 21, pp. 145-148; Oct. 28, pp. 163-166, 170). The author considers problems which will confront the enamelling industry at the end of the war. If sheet iron pressings tend to replace castings and larger sheet iron components are constructed, larger pickling and spraying equipment will be needed. There will be a very large demand for new kitchen equipment both for new houses and to replace worn-out equipment; in this, enamelled material will play an important part. Should the pressed-steel bath replace the cast-iron one, this might well result in the end of the old dusting process. Extensions of the application of enamelling will be found in fluorescent-tube reflectors, enamel signs, coach fittings and shop-front decoration. On the technical side, the war has stimulated efforts to improve opacity without using tin oxide, and this has been done by preparing self-opacifying frits. Con-

siderable improvements in acid-resisting enamels have been made. From a production point of view, it is best to finish only in acid-resisting enamels, and to obtain colour and density with non-acid-resisting enamels of a firing temperature similar to that of the final acid-resisting enamel. The final spray of acid-proof enamel need not exceed 0·002 in. in thickness.

**A New Test for Measuring Enamel Slip Consistency.** G. T. O. Martin. (Institute of Vitreous Enamellers : Foundry Trade Journal, 1943, vol. 71, Nov. 18, pp. 221–224, 228). In the vitreous enamelling of steel sheet the adjustment of the consistency of the enamel slip is a critical factor in obtaining a uniform ground coat of the correct thickness. A new method of rapidly determining this consistency is described. The method is based on the fact that, when the slip approaches the correct consistency, a small glass plate dipped in it and drained is almost, but not quite, opaque. From laboratory and works tests a simple apparatus was developed. This consists of a box in the front of which is a frame carrying a set of glass plates of different opacity matched with slips of different consistency values obtained by the former steel-plate method, and a space for the glass plate from the slip to be tested ; behind the frame is a mercury vapour lamp and a suitable reflector. On switching on the lamp the opacity of the test glass plate can be readily compared with that of the standard glasses.

**Mechanics of Enamel Adherence : XV. Influence of Cobalt and Nickel Oxides on Metal Precipitation at Ground-Coat/Iron Interface.** R. M. King. (Journal of the American Ceramic Society, 1943, vol. 26, Oct., pp. 358–360). The method previously described (see Journ. I. and S.I., 1943, No. II., p. 29 A) for determining metal precipitation during ground-coat firing on sheet iron has been refined and used in a quantitative study in which the influence of cobalt and nickel oxides on this precipitation were compared. Nickel oxide had the stronger action, even when the ratio of cobalt oxide to nickel oxide was 3 to 1.

**Developments in Thermal Technique as Applied to Vitreous Enamelling Processes.** J. Fallon. (Institute of Vitreous Enamellers : Foundry Trade Journal, 1943, vol. 71, Dec. 16, pp. 305–309). The advantages and limitations of batch and continuous furnaces for vitreous enamelling are discussed. The great problem in the continuous furnace, the heating of which is relatively simple, is the provision of a transport system suitable for handling goods at elevated temperatures with minimum depreciation. Split-crown units carrying work suspended on drop hangers are best suited to extremely high capacity plant of considerable length. For a plant of medium capacity, a simple live-roll conveyor unit, transporting perrit bars of standard size, or of special size to afford suitable grouping of the load, comes nearest to the ideal solution of the furnace problem. Where multiple stacked goods are to be subjected to the drying process, infra-red ray equipment is not a feasible or

economic proposition and is not likely to displace either the static, continuous straight line or camel-back drying oven.

**Electrostatic "Detearing."** H. P. Ransburg. (American Gas Association : Steel, 1943, vol. 113, Aug. 9, pp. 106, 131-132). When metal articles are dipped in synthetic resin or other protective solutions and then allowed to drain, blobs or "tears" of the solution form at the points where it drains off; the removal of the final blobs in a manner which leaves a smooth and even surface is a problem which has been solved in a manner described by the author. The "drain-off points" are subjected to an electrostatic field by means of an electrode charged at a very high voltage.

## PROPERTIES AND TESTS

(Continued from pp. 59 A-66 A)

**Statistical Analysis of Inspection Results.** H. H. Fairfield. (Engineering Journal, 1943, vol. 26, Sept., pp. 492-501). In the inspection of war materials great numbers of inspection tests are performed, and much useful information can be obtained by analysing large numbers of test results. In this paper, which serves as an introduction to the science of statistics, the principles of statistical analysis are explained and some simple examples are given. By the proper application of these methods the number of rejects is frequently decreased and the number of man-hours spent on inspection can be lowered.

**Notched Bar Tensile Test Characteristics of Heat Treated Low Alloy Steels.** G. Sachs, J. D. Lubahn and L. J. Ebert. (American Society for Metals, Oct., 1943, Preprint No. 26). The following factors influencing the tensile strength of notched specimens of high-strength low-alloy steels have been investigated: (1) Variations in surface conditions at the root of the notch; (2) variations in notch radius; and (3) eccentricity of loading. The first part of the investigation concerned the notch radius. The transverse elastic strain, the notched-bar strength and ductility of a steel with a tensile strength below 200,000 lb. per sq. in. were almost independent of the notch radius between zero and  $\frac{1}{32}$ -in. radius. Only when the notch radius became rather large did the notched-bar strength decrease with increasing radius, whilst the notched-bar ductility simultaneously increased. The notched-bar strength of a steel of high tensile strength increased with increasing notch radius because of the smaller concentration of stress in the notched section. In the second part of the investigation tensile tests with a special eccentric fixture were carried out. The superposition of bending on tension in general reduced the notched-bar strength by amounts

which increased with increasing tensile strength of the steel and with increasing eccentricity of loading. Above a certain degree of eccentricity, the notched-bar strength of a steel decreased with increasing strength level. The results of the notched-bar tensile tests confirmed previous conclusions that a sharp notch severely embrittles any heat-treated steel.

**The Strength of Heat Treated Alloy Steel Bolts.** G. Sachs, P. S. Cole and R. A. Roth. (American Society for Metals, Oct., 1943, Preprint No. 27). An investigation of the strength of heat-treated 3.5% nickel steel bolts is reported. Bolts in the as-quenched state showed brittle fractures under the head at low and widely scattered test loads, thus indicating greater notch sensitivity at this point than in the threads. Failures under the head can be prevented by making a radius from the shank to the head. Superimposed bending by inserting a 10° wedge or shim caused brittle fractures at considerably reduced loads. With a shim under the head, brittle fractures occurred under the head if the bolt had been tempered at below 425° C., or if the tensile strength was above 160,000 lb. per sq. in. With a shim under the nut, failures occurred at very low loads by stripping of the threads. Only after tempering at above 650° C. did the thread attain the same strength when tested with or without a shim. Bolts of this nickel steel may be heat-treated to a tensile strength of 250,000 lb. per sq. in. if the straining in service is in pure tension, but 175,000 lb. per sq. in. is the maximum safe limit if bending is superimposed.

**The Yield Point in Bending and the Stress Distribution in Bars and Tubes in Plastic Bending.** L. Bernhult. (Jernkontorets Annaler, 1943, vol. 127, No. 10, pp. 491-533). (In Swedish). Many investigators have found that the yield point in bend tests differs from that in tensile tests. Values obtained by X-rays have been different for the two types of test, but more recent X-ray work as well as other investigations support the view that the yield point in bending is no higher than that in tensile tests. There is, however, an apparent increase in the yield point in bending which depends on the shape of the section in that the greater the concentration of material round the neutral axis, the greater is the value of the apparent yield point. By assuming that a bent beam consists of an infinite number of lamellæ, each of which behaves like a bar in tension or in compression, a reason is found for the fact that no actual increase in the yield point takes place in bending. The stress distribution in the bent bar or beam is determined by the tensile properties of the steel in question. The shape of the stress distribution curve across the section will vary, depending on whether the material has an upper yield point or whether there is no sharply defined yield point. The bending-moment curve is a straight line up to the point where the plastic and elastic moments are of equal value. Experiments in the cold-rolling of bars and tubes reported in this paper show that, when the moment in the plastic range begins

to exceed that in the elastic range, the curve deviates sharply from the straight line. In order to obtain information from which the rolling pressure and the effects of cold-rolling could be determined, calculations are presented covering that part of the bending-moment curve between the limit of proportionality in bending and the point corresponding to the fully plastic state across the section (the yield point in bending) for tubes of different ratios of internal to external diameter. It is shown that bars and tubes should be straightened within this stress range.

**Peened Surfaces Improve Endurance of Machine Parts.** J. O. Almen. (*Metal Progress*, 1943, vol. 43, Feb., pp. 209-215, 270). From an investigation of the causes of failure of gear teeth it is shown that either design or the finishing processes lead to fatigue failures much more often than defects in the quality of the steel; consequently laboratory fatigue tests on perfectly finished specimens are of little value in determining service life. The finish-machining or grinding which follows rough-machining rarely goes deep enough to remove all the metal containing residual stresses. Such residual stresses should be removed by heat treatment or mechanical means. It is advantageous to convert residual tensile stresses at the surface into compressive stresses; this can be done by a peening operation such as hammering, swaging, shot blasting or tumbling. In such cases the tension stress in the surface layer is reduced by the amount of the compressive prestress, and, since fatigue failure starts only under tensile stress, the endurance of the surface layer is increased. Föppl has shown that the fatigue fracture in cold-rolled specimens does not originate at the surface, but in the material below the prestressed layer. The amount of stress and depth of the stressed layer may be calculated from measurements of the curvature of test strips which are fastened on a heavy flat block, peened and then released; the surface is then honed in successive stages until the strip is again straight and the depth of metal removed is that of the stressed layer.

**How to Estimate Hardening Depth in Bars.** J. L. Lamont. (*Iron Age*, 1943, vol. 152, Oct. 14, pp. 64-70). Diagrams based on the Jominy end-quench hardenability test are presented and explanations are given of their application to predict: (1) The severity of quench when the cross-sectional hardness distribution is known of a single bar of the same steel quenched under the desired quenching conditions; (2) the diameter of round bars having a desired hardness at any point between the centre and surface, for a predetermined severity of quench; (3) the cross-sectional hardness distribution in a round bar of a given size for a predetermined severity of quench; (4) the dimensions of square bars, flat bars and the thickness of plates having a desired hardness at the centre for a predetermined severity of quench; and (5) the hardness at the centre of square bars, flats and plates for a predetermined quench severity.

**Hardness Testing with the Barcol Impressor.** J. H. Hruska. (*Iron Age*, 1943, vol. 152, Oct. 14, pp. 84-87). Particulars are given of the Barcol impressor hardness testing instrument. The penetrator consists of a hardened steel point ground to 0.00625 in. in dia. with an included angle of 24°; this fits in a hollow spindle and is held down by a spring loaded plunger. The instrument is only 5½ in. long and weighs about 12 oz. A leg at the back is first set against the surface to be tested and a pressure of about 16 lb. is applied by hand to the impressor housing. The depth of penetration is transmitted by levers to the spindle of a 1½-in. pointer.

**Effect of Time, Temperature and Prior Structure on the Hardenability of Several Alloy Steels.** J. Welchner, E. S. Rowland and J. E. Ubben. (*American Society for Metals*, Oct., 1943, Preprint No. 24). In view of the lack of sufficient quantitative information on the effects of time at quenching temperature and of quenching temperature and prior structure on the hardenability of steels, a series of tests was made using five low-alloy chromium-nickel-molybdenum steels of low and medium carbon content. The prior structures were varied from fully spheroidised to oil-quenched, the holding times ranged up to 4 hr. and the temperatures from which specimens were quenched ranged from 790° to 870° C. The steels in the medium carbon range reacted essentially alike. The spheroidised and annealed prior structures were very sensitive to the holding times employed, yielding hardenability values far below those expected with the shorter holding times. The exact size, shape and distribution of the carbides, more than any other single factor, govern the success or failure of quenching treatments when the holding time before quenching is short. From the results obtained on the higher-alloyed medium-carbon steels, it appears impossible to predict the hardness traverse of production parts treated from readily machinable prior structures unless the hardenability test is also conducted under reasonably equivalent conditions of time, temperature and prior structure.

**Steel Division Committee on Magnetic Tests Reports Results from Questionnaire.** (*American Foundryman*, 1943, vol. 5, Sept., pp. 2-3). A report is presented on the answers to a questionnaire on the magnetic-powder testing of castings which was submitted to members of the American Foundrymen's Association. Of those who replied, 57% stated they would accept orders stipulating magnetic inspection. Most of those who would not accept orders subject to this inspection were not familiar with the method. It appeared from the answers that the indications produced by the magnetic powder are not all due to defects and a great deal of unnecessary chipping of castings is caused.

**A New Method of Sorting Steels.** R. J. Brown and J. Bridle. (*Engineer*, 1943, vol. 176, Dec. 3, pp. 442-444). Apparatus for measuring the magnetic properties of steel and employing a cathode-

ray oscillograph has been used for sorting bars of different steels which have become mixed, but such apparatus is not sufficiently robust for workshop use. In this paper a simplified form of equipment embodying an amplifier, but with a cathode-ray tuning indicator instead of the oscillograph, is described. The magnetic differences between a standard specimen and the sample, which must be of the same cross section, are measured under the influence of equal alternating magnetic fields. Examples of steels which have been satisfactorily sorted are given. The apparatus is portable, inexpensive and easily constructed.

**Electronic Sorting and Testing.** (Iron Age, 1943, vol. 152, Nov. 4, pp. 57-58). Some particulars are given of the Cyclograph, an electronic apparatus with which non-destructive tests on ferrous and non-ferrous metals can be made. The piece to be tested is held in a case which is really a tuned pick-up coil. Changes in the properties of the steel cause variations in the core loss of the coil and these alter the pattern of the cathode-ray oscillogram displayed on a screen. When large quantities of parts are to be tested the machine can be adapted to automatic sorting at speeds as high as 5 pieces per sec.

**Creep Strength, Stability of Microstructure and Oxidation Resistance of Cr-Mo and 18-Cr/8-Ni Steels.** R. F. Miller, W. G. Benz and M. J. Day. (American Society for Metals, Oct., 1943, Preprint No. 37). Investigations of the effect of heat treatment on the creep strength and stability of microstructure of several chromium-molybdenum and chromium-nickel steels at 1000° and 1100° F. over a period of 3000 hr. showed that at 1100° F. the creep strength of the former steels is substantially the same over the chromium 2% to 9% range, that the stability of chromium-molybdenum steel (with chromium 5%) is increased by adding titanium or columbium, and that that of 18/8 steel with columbium is greater than that of 18/8 steel with or without titanium. A period of 3000 hr. at 900° F. produced no observable change of microstructure except in pearlitic 0.5%-carbon/molybdenum steel, but at 1000° F. there was a marked change in all the carbon-molybdenum steels; chromium stabilised the structure, little or no change being visible in the chromium-molybdenum steels after 3000 hr. at 1100° F. The resistance to oxidation of the carbon-molybdenum steels in air for 1000 hr. at 1100° and 1400° F. was about the same as that of plain carbon steel, and was not appreciably improved by up to 3% of chromium or up to 0.75% of silicon; a further increase in either chromium or silicon was beneficial. At 1700° F., all the carbon-molybdenum and the chromium-molybdenum steels were severely attacked.

**Creep and Heat Resistant Steel Castings.** F. Schulte. (Iron Age, 1943, vol. 152, Sept. 30, pp. 54-58; Oct. 7, pp. 64-68). An English translation is presented of a paper which appeared in Stahl und Eisen, 1942, vol. 62, May 7, pp. 389-397 (see Journ. I. and S.I., 1942, No. II., p. 123 A).

**Research into Hydrogen Embrittlement.** D. W. Rudorff. (Iron and Steel, 1943, vol. 17, Nov., pp. 136-139, 170). The author reviews some recent research work on the embrittlement of steel by hydrogen, in particular, that of Bastien which appeared in *Revue de Métallurgie*, 1941, vol. 38, p. 225 *et seq.* Tests were made in an Amsler machine to establish the number of bends required to fracture a 2-mm. dia. wire after pickling under various conditions. Embrittlement due to hydrogen diffusion proceeds rapidly only during the first hour of immersion; after 6 hr. no further deterioration in the bending properties occur. The recovery from embrittlement on exposure is much slower with increasing moisture in the air. After pickling the wire for 5 min. in a 10% hydrochloric acid solution the embrittlement is confined to a surface layer 0.15-0.2 mm. deep. Rapid and complete disappearance of embrittlement is effected by immersing the pickled material in cold water. Complete recovery does not take place if the amount of hydrogen diffused into the material exceeds a certain critical value. Rapid and complete disappearance of embrittlement is obtained by exposing the pickled material to air at 100-300° C.

**Special Addition Agent Steels.** R. B. Schenck. (Iron Age, 1943, vol. 152, Oct. 14, pp. 88-91). Data are presented on the mechanical properties, hardenability and grain size of managanese steel bars treated during manufacture with different addition agents containing various combinations of aluminium, boron, calcium, silicon, titanium and zirconium.

**Some Effects of Heat Treatment on Low Alloy Titanium Steels.** G. F. Comstock. (American Society for Metals, Oct., 1943, Preprint No. 23). Most of the available information on titanium steels has been obtained from small ingots converted into bars without the same high-temperature soaking-pit treatment as is generally given to full-size commercial ingots. In this paper the influence of this treatment on a 0.13% carbon steel, a 0.37% carbon steel, a low-alloy chromium-molybdenum steel and a 1.24% manganese steel, all containing titanium, is discussed. The increased strength produced by titanium can be utilised in steels in the as-rolled condition, or when stress-relieved at sub-critical temperatures, because the billets are generally heated to above 1095° C. for rolling, and quenching is not required to retain the titanium in its strengthening form. Without mechanical working after the heating, the steel is coarse-grained and may have a low impact value. Normalising at between the critical range and about 1095° C. inhibits the strengthening effect of titanium, but the ductility and impact value are improved.

**An Emergency Heat Resistant Alloy.** P. Gordon, M. Cohen and R. S. Rose. (American Society for Metals, Oct., 1943, Preprint No. 34). An account is given of investigations of nearly one hundred alloy steels; these were undertaken to develop heat-resisting alloys with low contents of the metals now difficult to obtain. The work

included melting, casting, bend and tension tests at room temperature, tension and creep tests at up to 870° C., and determination of the resistance to scaling in air and sulphur-bearing gases at 760° and 870° C. The most promising results were obtained with alloys containing carbon 0·30–0·35%, silicon 2%, chromium 10–12%, nickel in the range 4–10% and manganese in the range 2–12%, with the nickel and manganese supplementing each other and in amounts producing a wholly austenitic alloy. Numerous tables and curves from the test data are presented. These show, among other things, the relation between the nickel and manganese contents and the ductility at different chromium levels, and the amounts of manganese and nickel necessary to produce wholly austenitic alloys at different chromium levels. Comparisons are made between the properties of these "emergency" alloys and those of 18/8 and 25/12 chromium-nickel steels.

**User Report No. 21 on Experience with NE (National Emergency) Alloy Steels.**

F. Born. (*Steel*, 1943, vol. 113, Nov. 8, p. 110). Some particulars are given of the successful substitution of Steel N.E. 9445 for steel S.A.E. 2340 for making cams and brake shaft forgings.

**Boron Assumes a Position of Importance as an Alloying Element in Steel.** A. F. Macconochie. (*Steel*, 1943, vol. 113, Oct. 18, pp. 106–108, 129). Some recent publications on the effect of alloying steel with boron are reviewed and the compositions of four deoxidisers containing small percentages of boron are given.

**Screw Machine Steels.** A. S. Jameson. (*Iron Age*, 1943, vol. 152, Oct. 28, p. 69). Further tables of the mechanical properties of medium-carbon sulphurised free-machining steels are presented (see p. 63 A).

**Alloy Steel Specifications. . . . Based on Pet Analysis or Performance?** G. van Dyke. (*Iron Age*, 1943, vol. 152, Oct. 14, pp. 71–73). It is suggested that the present trend to specify steels to narrower and narrower limits of analysis should be stopped by substituting wider analysis limits combined with a hardenability test. The advantages of this scheme are discussed. A procedure adopted by an alloy-steel manufacturer is described for giving detailed hardenability data for particular steels; this involves four Jominy end-quench tests, one in the ordinary way, and the others on specimens which have been tempered at 1000°, 1100°, and 1200° F. respectively.

**An Optimum Silicon Range in Plain and 2·0 per Cent Chromium Cast Irons Exposed to Elevated Temperatures.** C. O. Burgess and R. W. Bishop. (*American Society for Metals*, Oct., 1943, Preprint No. 36). Tests were made to determine the effect of increasing quantities of silicon up to 7% on the oxidation resistance of ordinary cast iron and of 2%-chromium cast iron when heated at up to 800° C. for periods up to 500 hr. Both plain and chromium-bearing irons developed the maximum resistance to growth and oxidation in the relatively narrow silicon range of 3·0–4·5%.

**High-Si Acid-Resisting Cast Iron.** J. E. Hurst. (Institute of British Foundrymen : Foundry Trade Journal, 1943, vol. 71, Dec. 9, pp. 283-289; Metallurgia, 1943, vol. 29, Nov., pp. 21-25). The properties of high-silicon cast iron are discussed. Increasing the silicon content raises the resistance to acid attack. In the case of boiling 20% sulphuric acid a critical value is reached at 14.25% of silicon, above which there is no increase in the corrosion resistance. With boiling 70% nitric acid the critical value is slightly lower at about 12.5% of silicon. Hydrochloric acid attacks the iron more strongly than sulphuric and nitric acids, but adding molybdenum improves the resistance of the iron to the first-named acid. The attack on silicon iron by concentrated and dilute phosphoric acids is negligible at room temperature. Commercial 15%-silicon acid-resisting iron has a strength value of approximately half that of a good grey cast iron. A diagram for 15%-silicon iron containing 0.65% of manganese is presented which shows the equilibrium conditions over a range of carbon contents of 0.3-0.9%. In the range of carbon 0.25-0.4%, the castings are subject to hot tears. At every stage in the manufacture of silicon-iron castings precautions against the accidental introduction of hydrogen-bearing materials into the molten metal must be taken, so that there will be no gas bubbles in the castings. At temperatures in the 700-800° C. range, silicon iron has a large degree of plasticity and toughness as compared with its properties at normal temperatures. At above 800° C. excessive softening takes place. Oxy-acetylene welding is better than electric welding for silicon-iron castings.

**Gear Steels in Mining Machinery.** S. H. Frederick. (Iron and Coal Trades Review, 1943, vol. 147, Nov. 12, pp. 753-754). Recommendations on the selection of steels for gears in mining machinery are made. For gears operating at low speeds under light to medium loads, an oil-hardened 0.40-0.45% carbon steel is quite satisfactory. For high-speed gears transmitting heavy loads a 0.35-0.40% carbon steel alloyed with 1.75% of nickel and 1.25% of chromium, oil-hardened and tempered at 200° C., has a tensile strength of 110-120 tons per sq. in. and gives excellent results; but for small pinions the tempering temperatures should be increased to 450° C., which lowers the tensile strength to 85-90 tons per sq. in. while increasing the toughness. Data on case-hardened gears are also given.

## METALLOGRAPHY AND CONSTITUTION

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(Continued from pp. 66 A-69 A)

**Electrolytic Polishing of Metals.** S. Wernick. (Journal of the Electrodepositors' Technical Society, 1943, vol. 18, pp. 103-120). See Journ. I. and S.I., 1943, No. II., p. 132 A.

**A High Temperature X-Ray Analysis Camera.** E. A. Owen. (Journal of Scientific Instruments, 1943, vol. 20, Dec., pp. 190-192). A new design of X-ray camera for use with specimens at temperatures up to 1000° C. is described. The specimen, in fibre form, is situated at the centre of an electric furnace which is so mounted that it can be removed without disturbing the specimen, and the whole is enclosed in a chamber which can be evacuated. The camera is mounted outside this chamber and can be removed for processing the film, and then replaced without disturbing the rest of the apparatus. Reproductions of the structure-spectra of pure iron, taken when the material was maintained at 800° and 950° C. *in vacuo*, are presented.

**Limitations of Radiography as an Inspection Method.** V. I. E. Wiegand. (Metal Progress, 1943, vol. 43, Feb., pp. 229-232). A catalogue is presented of the characteristics of material to be X-rayed and of the X-ray equipment which adversely affect the results obtained; some proper and some unsuitable applications of metallurgical X-ray work are also cited.

**Determining the  $Ac_3$  Critical Point in Iron by a Grain Elimination Method.** J. K. Desmond. (Transactions of the American Society for Metals, 1943, vol. 31, pp. 1-7). Experiments are described in which specimens of low-carbon nickel-chromium iron were strained by cold-hobbing and annealed at different temperatures. When annealed at 675° C., which is well below the  $Ac_3$  point, large ferrite grains were developed in strained areas at some distance from the hobbed surface. By increasing the annealing temperature in stages a point was reached at which these large grains disappeared. This method is suggested as a method of determining the  $Ac_3$  point. The  $Ac_3$  point was found to be 851° C. for the above alloy.

**A Quantitative Study of Austenite Transformation.** R. A. Flinn, E. Cook and J. A. Fellows. (Transactions of the American Society for Metals, 1943, vol. 31, pp. 41-66). A detailed description is given of a dilatometer apparatus incorporating a photocell and recording device with which a complete record of changes in length could be obtained of a specimen from the time it was immersed in a lead bath to the time of withdrawal. This was used to study the three modes of austenite decomposition, namely: (a) The transformation to pearlite, to ferrite and pearlite, or to cementite and pearlite; (b) the intermediate transformation to acicular structures; and (c) the transformation to martensite. Graphs were prepared from the dilatation curves to show a method for locating the  $M$  point (at which transformation to martensite begins), and the progression of this transformation with decreasing temperature in steels of different carbon content. The data presented emphasise the narrow temperature range for the isothermal annealing of high-alloy steels, the sluggishness of the later portions of the acicular transformation and the instantaneous nature of the martensite reaction with its high volume change.

**The Isothermal Transformation of Case-Carburized S.A.E. 4815.**

J. R. Cruciger and J. R. Vilella. (American Society for Metals, Oct., 1943, Preprint No. 17). Isothermal transformation diagrams are presented for steel S.A.E. 4815 in the uncarburised and in the case-hardened states (before case-hardening the steel tested contained carbon 0.16%, manganese 0.52%, silicon 0.27%, nickel 3.36% and molybdenum 0.19%) and these are discussed in the light of the structures observed in several micrographs. The  $Ae_1$  point was  $675^{\circ}$  C. and the martensite point (the highest temperature of instantaneous martensite formation) was determined by the method of A. B. Greninger and A. R. Troiano (see Journ. I. and S.I., 1940, No. I., p. 50 A). The first evidence of tempered martensite, indicating that the martensite point had been found, appeared in the specimen quenched in a bath at  $95^{\circ}$  C. The main effect of carburising is to retard the rate of transformation, *i.e.*, the pair of curves for the beginning and end of the transformation in the case lie to the right of the corresponding pair for the uncarburised steel, particularly at the lower temperature levels. At  $595^{\circ}$  C. and above, the curves for the beginning of the transformation to pearlite in both carburised and uncarburised steels very nearly coincide. Although the curves for the uncarburised steel lie above the corresponding curves for the carburised steel, the knee occurs at approximately the same temperature.

**Pseudomorphs of Pearlite in Quenched Steel.** O. W. Ellis. (American Society for Metals, Oct., 1943, Preprint No. 30). Further evidence is provided of the rapidity with which steel can be raised above the critical range by induction heating. It is shown that the point is almost reached where steel, after induction heating, can be quenched before any change has occurred in it other than that from  $\alpha$ -iron to  $\gamma$ -iron. It is thus possible to obtain, by rapid induction heating and immediate quenching, pseudomorphs of structures purposely formed in steel before heating and quenching. It is suggested that such pseudomorphic structures may have properties worthy of fuller study and of application in engineering, and that in future, on this account, less stress should be placed on ensuring that diffusion occurs during induction heating.

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**CORROSION OF IRON AND STEEL**

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(Continued from pp. 70 A-71 A)

**Progress in the Corrosion Research Section at Cambridge University.** U. R. Evans. (Iron and Steel Institute, 1944, this Journal, Section I). The paper summarises results of investigations published since 1935 by twenty-four experimenters in sixty-four papers scattered through different journals. The research policy

has been to study scientific causes and then to apply the results to practical problems; success or failure attending the applications provides a check on the accuracy of the scientific conclusions.

The electric currents flowing over the surface of metal corroding in salt solution have been measured, and found strong enough to account for all or nearly all the attack actually produced; corrosion is seen only at those points which the electrical apparatus indicates as anodic, and everything points to an electrochemical mechanism. Numerous measurements of "probability" and "conditional velocity" have been made, and the distinction between these two conceptions clears up many points which have hitherto appeared paradoxical; it shows why, on iron partly immersed in a salt solution, the water-line zone is immune in the early stages and strongly attacked later, and indicates that oxygen is at once a stimulator in increasing conditional velocity and an inhibitor in diminishing the probability. Sulphides in the metal or hydrogen sulphide in the liquid stimulate, under many circumstances, both the probability and the conditional velocity; the presence of copper in the steel, or tin salts in the liquid, largely counteracts the bad effect of sulphur, by fixing it in a stable form.

Electrochemical principles, borne out by practical experiments, indicate that anodic inhibitors may be "dangerous," since they localise and intensify attack if added in insufficient amounts. An experimental classification of inhibitors as "anodic" and "cathodic" has been carried out, and many attempts have been made to find an inhibitive system which would be both safe and efficient. The latest results are encouraging.

About 3000 painted steel specimens have been exposed out-of-doors at different stations, and certain combinations of coats have given good protection over seven years in London; the presence of partly removed mill scale is prejudicial to good results. New compositions, including zinc-rich organic paints, emulsion paints and inorganic (cementiferous) paints, are being developed for special purposes. Laboratory investigations regarding the causes of blistering and the anti-corrosive action of certain lead compounds are in progress.

Much work has been conducted on steel covered with metallic coats, including galvanised iron and tinplate; the behaviour of the latter in canning varies with the composition of the steel basis.

In researches on corrosion-fatigue, new methods have been developed for feeding the corrosive liquid on to the specimen, giving a sharp water-line. The results show that corrosion-fatigue life can be greatly prolonged by contact with zinc or by paints pigmented with metallic zinc.

Electrochemical methods of estimating the thickness of thin films have been developed and compared with other methods. These have been used to study the thicknesses of interference-colour films, and also to follow the oxidation of iron exposed at ordinary

temperatures (where the oxide remains invisible) as well as at higher temperatures. Methods have been worked out for transferring the films to celluloid. Several theoretical papers have been written on the laws governing film growth, and these largely academic lines of thought have led to a method known as "selective oxidation," which has greatly reduced the high-temperature oxidation of copper and the low-temperature tarnishing of silver. It has not yet been applied to ferrous metals.

**Protection against Caustic Embrittlement by Coordinated Phosphate-pH Control.** T. E. Purcell and S. F. Whirl. (Electrochemical Society, Apr., 1943, Preprint No. 83-25). The results of tests with embrittlement detectors on boilers in actual operation under varying conditions of water treatment, pressure, time and specimen composition are presented and discussed. A new method of water treatment to prevent caustic embrittlement is proposed. No inhibitor is used but a trisodium phosphate solution is added to maintain "phosphate alkalinity" of the boiler water instead of "caustic alkalinity". The pH value and  $\text{PO}_4$ -ion concentration is controlled in accordance with a curve relating the pH value to the  $\text{PO}_4$ -ion concentration in pure trisodium phosphate solutions. The method is a practical one and does not involve new methods of analysis. It is particularly applicable to high-pressure boilers.

## BOOK NOTICES

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American Society for Testing Materials. "*ASTM Specifications for Steel Piping Materials.*" 8vo, pp. vi + 255. Philadelphia 1943 : The Society. (Price \$1.75.)

This publication contains all the specifications for carbon-steel and alloy-steel pipe and tubing issued by the American Society for Testing Materials through the work of its Committee A-1 on Steel. The specifications cover material used to convey liquids, vapours, and gases at normal and elevated temperatures; still tubes for refinery service are covered and specifications are included for heat-exchanger and condenser tubes. A number of the widely used standards give requirements for boiler and superheater tubes. To make the volume complete there are also included specifications covering castings, forgings, bolts and nuts used in piping and related installations. To aid in expediting procurement and in conserving critical and strategic elements many emergency alternative provisions have been issued. These provisions, printed on coloured slips, are incorporated in the book.

Low, D. A. "*A Pocket-Book for Mechanical Engineers.*" Edited by B. B. Low. New Edition Revised. Sm. 8vo, pp. xii + 778. Illustrated. London 1943 : Longmans, Green & Co. (Price 15s.)

The edition published in 1942 soon became out-of-stock and opportunity has been taken to make a few changes. The Equivalent Temperatures on the Fahrenheit and Centigrade Scales now cover a wider

range, and the notes on the Practical Measurement of Temperature have been extended. The information in the Boiler section replaces older matter, and the section on Compressed Air has been revised.

**Society of Chemical Industry.** "Reports of the Progress of Applied Chemistry." vol. xxvii—1942. 8vo, pp. 545. London : The Society. (Price 20s.)

This volume consists of surveys by leading authorities on the progress in 1942 of Applied Chemistry in its numerous branches. The reports contained in the present volume, many of which are of interest to those engaged in the manufacture of iron and steel, are as follows:—General Plant and Machinery, by F. Rumford; Fuel, by J. Hiles and R. A. Mott; Gas, Destructive Distillation, Tar, and Tar Products, by F. J. Dent, A. Key, L. A. Moignard and R. Long; Mineral Oils, by W. W. Goulston; Intermediates and Colouring Matters, by R. Fraser Thomson; Fibres, Textiles, and Cellulose: The Protein Fibres, by C. S. Whewell; Cellulose Textile Chemistry, by J. T. Marsh and F. C. Wood; Pulp and Paper, by J. Grant; Acids, Alkalies, Salts, etc., by P. Parrish and F. C. Snelling; Glass, by W. M. Hampton and R. E. Bastick; Ceramics, Refractories and Cements, by H. W. Webb; Iron and Steel, by W. H. Hatfield; Non-Ferrous Metals, by E. S. Hedges; Electro-Chemical and Electro-Metallurgical Industries, by J. W. Cuthbertson; Fats, Fatty Oils, and Detergents, by T. P. Hilditch; Plastics, by Members of the Plastics Group; Resins, Drying Oils, Varnishes, and Paints, by Members of the Oil and Colour Chemists' Association; Rubber, by T. R. Dawson; Leather, by J. H. Bowes; Soils and Fertilisers, by A. G. Pollard; Sugars and Starches, by E. B. Hughes; The Fermentation Industries, by B. M. Brown; Foods, by E. B. Hughes and Collaborators; Fine Chemicals and Medicinal Substances, by N. Evers; Photographic Materials and Processes, by E. G. V. Barrett, D. J. T. Howe and J. W. Glassett; Sanitation and Water Purification, by J. Hurley.

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**AMERICAN SOCIETY FOR TESTING MATERIALS.** "Tables of Data on Chemical Compositions Physical and Mechanical Properties of Wrought Corrosion-Resisting and Heat-Resisting Chromium and Chromium-Nickel Steels." Prepared by R. Franks and F. LaQue for Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys. December, 1942. 8vo, pp. 43. Illustrated. Philadelphia, Pa, 1943. The Society. (Price \$1.25.)

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## ORES—MINING AND TREATMENT

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(Continued from pp. 37 A-39 A)

**Oregon Chrome Sands Yield to Magnetic Separation.** J. B. Hutt<sup>l</sup>. (*Engineering and Mining Journal*, 1943, vol. 144, Sept., pp. 62-65). Particulars are given of the plant used by the Krome Corporation for concentrating chromiferous sands in the black sand deposits of Coos County, Oregon. The chromic oxide content varies from 3% to 20%. The bed is about 15 ft. thick, and is worked by drag-line scrapers. A primary concentrate containing 25% of Cr<sub>2</sub>O<sub>3</sub> is produced by tabling, and this is sent to a large magnetic separation plant, where the Cr<sub>2</sub>O<sub>3</sub> content is brought up to at least 40%.

**New Type Concentrator Cuts Chromite Dressing Costs.** J. B. Hutt<sup>l</sup>. (*Engineering and Mining Journal*, 1943, vol. 144, Oct., pp. 68-70). A description is given of an ore concentration plant used by the Humphreys Gold Corporation in the recovery of chromite from the marine black sand deposits in Oregon. The sand contains 6% of Cr<sub>2</sub>O<sub>3</sub>, and the concentration is raised to 25% with a recovery of 90%. The interesting feature of the plant is the Humphreys spiral launder down which the washed material flows; in this, the chromite and gangue separate by the action of centrifugal force, the slower-moving chromite particles working towards the centre of the launder, and the coarser and lighter gangue travelling along the periphery.

**Beneficiation and the Supply of Mineral Raw Materials.** S. Mörtsell. (*Teknisk Tidskrift*, 1943, vol. 73, Dec. 18, pp. 585-592). (In Swedish). The history of the development of ore beneficiation, with special reference to Swedish iron ores, is reviewed.

**A Century and a Half of Development behind the Adirondack Iron-Mining Industry.** J. R. Linney. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 480-487). An illustrated historical review of the development of iron-mining and iron-making in the Adirondack Mountains from 1792 to the present time is given.

**Republic Steel's Operations at Port Henry, Mineville and Fisher Hill.** R. J. Linney. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 488-502). The Republic Steel Corporation in 1938 took over iron-ore properties in the Adirondacks at Mineville and Port Henry, where they now control mines, mills and sintering plants. Since then the Corporation have developed the mines, built a new wet concentrator and rebuilt the sintering plant, so that it is now in a position to supply one million tons of iron-ore concentrate per annum. A description of the mining, concentrating and sintering operations is given.

**Operations of the Chateaugay Division of Republic Steel, at Lyon Mountain.** W. J. Linney. (*Mining and Metallurgy*, 1943, vol. 24,

Nov., pp. 503–508). An illustrated description is given of the mining, concentrating and sintering operations for the magnetite ores at the Republic Steel Corporation's plant at Lyon Mountain in the northern foothills of the Adirondacks. The main entrance to the mine is by a shaft 8 ft. high and 24 ft. wide inclined at 63° and sunk to a depth of 2350 ft. The Chateaugay ore, as it is called, contains 25% of iron; by milling and magnetic concentration the iron content is brought up to 68%. This concentrate is mixed with 5½% by weight of granulated anthracite and a little water in a pug mill to prepare it for sintering. The mixture is spread evenly on the pallets of the sintering machine, which is 6 ft. wide and 82 ft. long, and is ignited by passing under an oil-fired ignition furnace, combustion being assisted by a downward current of air. The plant produces 58 tons of sinter per hr.

**Development and Operation of Clifton Mines, Hanna Ore Co.**  
G. B. Hunner. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 517–519). An account is given of the commencement of mining operations at the Clifton magnetite ore mine on the western slope of the Adirondack Mountains. Open-pit working has been in progress since 1941, and a vertical shaft is now being sunk. The beneficiation plant will include primary and secondary crushing, wet magnetic separation, milling and sintering.

**Geology of the Clifton and Parish Ore Deposits.** A. E. Walker. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 519–520). Some particulars of the geology of the magnetite-ore deposits at the Clifton mines, as well as at Parish near by, in the Adirondacks, are given. The Clifton ore bed is a member of a series of highly metamorphosed, siliceous, sedimentary, pre-Cambrian gneisses.

**Mining Methods at Clifton Mines.** F. W. Sutter. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 520–521). A description of the drilling and blasting operations at the open-pit workings on the Clifton magnetite ore beds is given.

**The Clifton Mill and Sinter Plant.** J. C. Durfee. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 521–522). Some details of the crushing, screening, magnetic concentrating and sintering operations at the Clifton mines in the Adirondacks, together with flow-sheets, are presented.

**Jones & Laughlin's Development at Benson Mines.** E. H. Robie. (*Mining and Metallurgy*, 1943, vol. 24, Nov., pp. 523–525). The work undertaken by the Jones and Laughlin Ore Co. in developing the magnetite-ore property at Benson Mines in the western Adirondacks is described. The mine will be worked as an open pit for some years. As mined, the ore contains 25–30% of iron, and this will be concentrated magnetically up to 60–65%. A plant to produce 400,000 tons of sinter per annum was planned, but at Government request the capacity is to be raised to 1,000,000 tons.

## REFRACTORY MATERIALS

(Continued from pp. 74 A-75 A)

**The Compound Merwinite ( $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ) and Its Stability Relations within the System  $\text{CaO}-\text{MgO}-\text{SiO}_2$ .** (Preliminary Report). E. F. Osborn. (Journal of the American Ceramic Society, 1943, vol. 26, Oct., pp. 321-332). Preliminary investigations on compositions between  $\text{Ca}_2\text{SiO}_4$  and akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ), between merwinite ( $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ ) and akermanite, and between merwinite and monticellite ( $\text{CaMgSiO}_4$ ) indicate that a field of merwinite appears on the liquidus surface of the system  $\text{CaO}-\text{MgO}-\text{SiO}_2$ , and that merwinite melts incongruently at  $1575^\circ\text{C}$ . to  $\text{Ca}_2\text{SiO}_4$ ,  $\text{MgO}$  and liquid.

**The Action of Alkalies on Refractory Materials. Parts XIII., XIV. and XV.** F. H. Clews, H. M. Richardson and A. T. Green. (Transactions of the British Ceramic Society, 1943, vol. 42, Nov., pp. 209-220). In Part XIII. an experiment is described which demonstrates that the expansion produced by the action of potassium chloride on a firebrick at  $1000^\circ\text{C}$ . is sufficient to cause cracking of the brick under appropriate conditions. In experiments described in Part XIV. a silica and a firebrick material were impregnated with various amounts of sodium and potassium salts and heated at  $1000^\circ\text{C}$ . for different periods. The transverse modulus at  $1000^\circ\text{C}$ . of the specimens was determined. The silica material suffered considerable reduction in strength through the fluxing action of the salts. The reduction in strength appeared to be correlated with the amount of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  that had combined with the brick, and with the increase in length. Sodium salts as a class caused a greater reduction in strength than the potassium salts. The presence of unchanged salt appeared to have little influence on the transverse strength at  $1000^\circ\text{C}$ . The firebrick material treated with sodium salts was markedly softened at  $1000^\circ\text{C}$ ., whereas the effect of the potassium was rather to cause weakening through embrittlement. The results have been correlated with phase rule and cone deformation data for the relevant portions of the  $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Na}_2\text{O}$  and  $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$  systems. In experiments described in Part XV. test-pieces moulded from mixtures of sodium aluminate with (a) calcined alumina, (b) sillimanite, and (c) china clay, were heated at  $1000-1400^\circ\text{C}$ ., and the changes in dimension measured. Expansions were observed under conditions when reaction without liquefaction could occur, and contractions were observed when the conditions allowed partial liquefaction.

**Refractories for Side-Blow Converters.** L. L. Gill. (Industrial Heating, 1943, vol. 10, Oct., pp. 1535-1544). The materials used and the construction of linings for side-blown converters are discussed. All stages in the manufacture of the silica bricks, fireclays

and ganister must be carefully controlled to ensure high quality. In lining the bottom, a ganister backing is first rammed next to the steel shell and three courses of brick are laid on this, the top course being set on the side edge. A method of strengthening the pouring lip in the hood is to leave  $\frac{1}{2}$  in. free of the rammed mix and to drive nails into the exposed end, leaving  $\frac{1}{2}$  in. of the nails protruding; the last  $\frac{1}{2}$  in. is then filled and rammed with ganister. When the iron to be refined is desulphurised in a ladle it is important that the basic slag should all be skimmed off before it is put in the converter; this prevents any chemical action between the slag and the silica brick converter lining.

**Some Properties of Heat-Setting Refractory Mortars.** R. A. Heindl and W. L. Pendergast. (*Journal of Research of the National Bureau of Standards*, 1943, vol. 30, Apr., pp. 303-310). A report is presented on the properties of twelve refractory mortars of the heat-setting type supplied by eight American manufacturers. The data given relate to the sieve analysis, Seger cone number, amount of mixing water required, trowelling and drying properties, strength at various temperatures, shrinkage and cracking tendency.

**Mottled Silica Brick, Facts, Fancies and Fallacies.** F. A. Harvey and C. L. Thompson. (*Journal of the American Ceramic Society*, 1943, vol. 26, Nov. 1, pp. 361-364). The literature on the causes and effects of coloration in silica bricks is reviewed and some tests on mottled and white bricks are reported. Although iron oxide is the colouring agent, variation in the amount in the normal range encountered in American practice has less effect than other factors on the production of mottled brick. It appears, however, that those ganisters higher in iron oxide are more likely to produce mottled brick. The dark-coloured areas of a mottled brick are usually not different from the light-coloured areas in iron oxide content. If the alumina content is abnormally low, below 0.5%, some of the bricks are almost certain to be mottled under normal manufacturing conditions. The two important properties of silica brick, namely, refractoriness-under-load and abrasion resistance, are not affected by mottling.

**Plant Investigation of Variables Affecting Color of Silica Brick.** J. S. McDowell. (*Journal of the American Ceramic Society*, 1943, vol. 26, Nov. 1, pp. 364-367). Experiments to ascertain the causes of mottling in silica bricks are reported. Bricks were made from batches containing increasing amounts of lime. After firing, bricks containing 0.5% of lime were not spotted, but were yellowish-brown throughout. Bricks containing 1.5-2.0% of lime had the white colour, slightly tinged with yellow, which was regarded as normal for well-burned brick. With about 2.2% of lime, some evidence of spotting was observed. The size and number of spots increased with increasing lime content until, with 3.5-4.0% of lime and no alumina, the bricks were dark brown throughout. Bricks with under 0.5% of alumina and 2% of lime were very susceptible to mottling in

firing, whereas those with 0·8–1·0% of alumina had little tendency to become mottled. Well-burned bricks in the outer portions of the kiln showed little tendency to become dark or spotted. Discoloration was greatest in bricks from those portions of the kiln having lowest draft or poor circulation of the kiln gases.

**Factors Influencing the Staining of Silica Brick.** L. J. Trostel. (*Journal of the American Ceramic Society*, 1943, vol. 26, Nov. 1, pp. 368–373). Experiments are reported the object of which was to ascertain how the conditions of firing affect the discolouration of silica bricks. The staining of silica bricks was found to occur in a critical temperature range of 900–1000° C. after holding for 4–6 hr. in an oxidising atmosphere. A study of the experimental data in conjunction with the  $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  system suggest that the mineral dicalcium ferrite is the colouring agent.

**Influence of Water Vapor on Silica Brick at High Temperatures.** F. A. Harvey. (*Journal of the American Ceramic Society*, 1943, vol. 26, Nov. 1, pp. 373–377). Tests to ascertain the effect of water vapour at high temperature on the properties of silica bricks are described. Bars cut from silica bricks of normal composition were subjected to the action of water vapour for 5 hr. at 1593° C.; they did not bend or soften, but did show a slight glaze on the surface. A 16-hr. laboratory test indicates that water vapour has little or no effect on American silica bricks of normal composition at temperatures up to 1593° C. This conclusion is not in agreement with that of A. E. Dodd (*see Journ. I. and S.I.*, 1936, No. II., p. 51 a), and indicates that the effects he observed were due to some cause other than water vapour.

**Mottled or Colored Silica Brick.** S. M. Phelps and R. W. Limes. (*Journal of the American Ceramic Society*, 1943, vol. 26, Nov. 1, pp. 378–387). Tests comparing the properties of uniform and of mottled silica bricks are reported. The following conclusions were reached: (1) The properties of the bricks are not affected by the mottling; (2) the mottled areas can be changed to the typical light cream colour by heat treatment; (3) any silica brick can be darkened by heating for a sufficiently long time at a suitable temperature; (4) a slow cooling rate after firing causes mottling, and fast cooling results in the normal cream colour; (5) sulphur does not appear to be a factor in the colour formation; (6) an extremely small variation in composition may account for the mottling; (7) there is evidence that the colour-forming proceeds through the development of wollastonite that may contain iron in solid solution which separates from it with heat treatment to form an iron-bearing mineral that is strongly coloured; and (8) small amounts of iron and alumina appear to be necessary to develop the colours occurring in mottled bricks.

**Refractories from the User's Viewpoint.** B. Thomas. (*Metallurgia*, 1943, vol. 29, Dec., pp. 61–65). Some considerations in the selection of refractory bricks for forging furnaces are put forward.

The hearth conditions, which will vary according to the fuel employed, should be considered first, then the temperature and the possibility of molten scale dripping from the charge, or of fusion of ash and clinker, and thirdly, whether the steel is heated in the combustion chamber or in a separate one. A cheap hand-made or wire-cut brick may often have better spalling resistance than one machine-pressed from the same clay, the reason being that the rougher surface allows greater freedom of movement under fluctuating thermal conditions.

**The Evaluation of the Properties of High-Temperature Insulating Materials.** L. R. Barrett, F. H. Clews and A. T. Green. (*Transactions of the British Ceramic Society*, 1943, vol. 42, Nov., pp. 220–234). The methods in vogue in Great Britain for the determination of the following properties of high-temperature insulating materials are discussed : (a) Thermal conductivity ; (b) porosity and bulk density ; (c) permeability ; (d) contraction on reheating ; (e) refractoriness-under-load ; (f) spalling resistance ; (g) resistance to the cutting action of flames and corrosive dusts ; (h) resistance to carbon monoxide attack ; and (i) the crushing and transverse strength when cold. The properties of seven representative British insulating bricks are given.

## PRODUCTION OF IRON

(Continued from pp. 42 A–44 A)

**The Spanish Iron and Steel Industry.** F. Millan. (*Revista de la Asociacion Nacional de Ingenieros Industriales de Espana : Nature*, 1943, vol. 152, Dec. 25, pp. 755–756). A brief account of the ore production and manufacture of iron and steel in Spain is presented. In 1940 the ore output was nearly 3,000,000 tons, but stocks accumulated so much that production in the first half of 1941 was reduced to 797,000 tons. The average iron content of the ore is now only about 40%. Manganese ore deposits are fairly considerable in places, but the output is very low ; in 1940 it was only 6850 tons, but it was hoped to raise this to 10,000 tons in 1943. In 1942 the pig-iron output was about 500,000 tons and that of steel 650,000 tons. The shortage of scrap for steelmaking is a difficulty, and a trial plant to study the Krupp-Renn process is to be put up near Bilbao.

**Mexico's Production of Iron Increased by Furnace at Monterrey.** (*Blast Furnace and Steel Plant*, 1943, vol. 31, Nov., pp. 1251–1254). A description is given of the new blast-furnace which was put in commission at Monterrey, Mexico, in July, 1943. The furnace has a hearth 15 ft. 6 in. in dia., and is designed to produce 500 tons of iron per day.

**Reconditioning of No. 1 Blast Furnace at Newcastle Steel Works.** (B.H.P. Review, 1943, vol. 20, Sept., p. 13). Brief particulars are given of the way in which one of the blast-furnaces of the Broken Hill Proprietary Co., Ltd., at Newcastle (New South Wales) was relined and enlarged. The hearth diameter was increased from 16 ft. to 17 ft. 9 in., the stockline diameter by 9 in., and the bosh top diameter by 1 ft. 6 in. The over-all capacity was increased by 11%.

**A Study of the Reducibility of Ores and Blast-Furnace Sinter.** W. O. Philbrook. (Blast Furnace and Coke Oven Association of the Chicago District and the Eastern States Blast Furnace and Coke Association : Blast Furnace and Steel Plant, 1943, vol. 31, Aug., pp. 890-897, 933, 934; Sept., pp. 1019-1024; Oct., pp. 1141-1147). The blast-furnace department of the International Harvester Co. investigated the factors affecting the reducibility of ores and sinters, including the mechanical problems of the operation of the sintering plant. Laboratory experiments were also made on small samples of ores and sinters with hydrogen as the reducing agent in an apparatus similar to that of M. Tenenbaum and T. L. Joseph (*see* Journ. I. and S.I., 1939, No. I., p. 207 A.). Percentage-reduction/time curves were plotted and a reducibility index was derived mathematically from the degrees of reduction achieved in 20 min. and 60 min. The chemical reducibility of the sinter decreased as the carbon content of the sinter mix before ignition increased. There was no relationship between the results of shatter tests on the sinter and the carbon content of the mix, or the reducibility of the mix, or the amount of moisture in the mix. The ores studied were more easily reduced than the sinters at temperatures in the 625-925° C. range. Observations at the sintering plant led to the belief that the amount and sizing of the returns have an important effect on the sintering operation, but this was not supported by an analysis of the experimental data. The use of basic open-hearth slag in the charge had no noticeable effect on the sinter plant operation ; the only effect on the sinter produced was to increase the lime and manganese contents and to decrease the proportion of iron. There was evidence of the tendency of an increase in the carbon content of the mix to promote an increase in the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$ .

## FOUNDRY PRACTICE

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(Continued from pp. 77 A-79 A)

**Cast Iron and the Foundry Industry.** J. E. Hurst. (Metallurgia, 1943, vol. 29, Dec., pp. 91-96). Some war-time applications of peace-time developments in British and American cast-iron foundry practice are reviewed ; these include : (1) The inoculation of molten

iron by late additions of ferro-silicon or of the higher-melting-point metals—molybdenum, tungsten and titanium—in conjunction with calcium silicide as a reducing agent; (2) a revised specification for a standardised impact test; (3) the use of the spectrograph in the routine analysis of cast iron; (4) basic linings for cupolas; and (5) the use of blind risers which are entirely surrounded by sand.

**Fuel Economy in the Iron Foundry.** C. Gresty. (*Foundry Trade Journal*, 1944, vol. 72, Jan. 13, pp. 31–34). Recommendations for reducing the coke consumption in iron foundries without loss of efficiency are made. The relationship between the nett output of castings and the weight of metal melted can be conveniently termed the yield, and even quite small increases in yield result in a considerable saving in fuel. As a cupola requires the same amount of bed coke each time it is put on, a small number of long runs is better than a large number of small runs. In a foundry requiring 60 tons of molten metal per week a saving of  $5\frac{1}{2}\%$  in the coke consumption is obtained by melting on five days each week instead of six. If a cupola has two rows of tuyeres, it is a simple matter to blank off the top one and to increase the size of the bottom row so that the total cross-sectional area remains the same. For core- and mould-drying stoves it is recommended that : (1) As few stoves as possible should be employed by filling those in use to capacity; (2) each stove should be fitted with a recording pyrometer, and a heavy line should be marked on the chart to indicate the desired temperature; (3) the fuel consumption of each unit should be ascertained and checked periodically; and (4) the heating unit should be maintained in an efficient manner and all flues kept clean.

**The Syphon Brick Method of Cupola Tapping.** E. R. Dunning. (*Foundry Trade Journal*, 1943, vol. 71, Dec. 30, pp. 341–344). A description is given of the syphon brick for tapping metal from the cupola. The primary object of the syphon brick is to eliminate the tapping and “botting up” of the cupola tap-hole each time metal is drawn off. With the syphon brick, the orifice from which the metal is drawn is continually open to the atmosphere, and the flow of metal is controlled by shutting the blast on and off. The ease of control permits the use of quite small ladles at the cupola, so that there is no need for redistribution from large to small ladles. The technique of operation and slagging procedure are described.

**Elements of Control in the Grey Iron Foundry.** B. Russell. (*Institute of Australian Foundrymen: Foundry Trade Journal*, 1944, vol. 72, Jan. 6, pp. 3–8, 2). The mechanical properties, damping capacity and wear-resistance of cast iron are reviewed and methods of controlling the production so as to obtain the optimum properties in grey iron are discussed. In order to obtain a matrix consisting solely of tough pearlite, it is necessary that the two components of pearlite, namely, cementite and ferrite, are present in the proportion of 1·7 to 1. Any excess of either constituent lowers its strength. The two main factors controlling the relative amounts of

ferrite and cementite are the chemical composition and the rate at which the casting cools. Silicon acts as a softener by promoting decomposition of the cementite into iron and graphite as the casting cools in the mould; raising the silicon content thus increases the amount of free ferrite at the expense of pearlite. Any excess of manganese over that required to combine with the sulphur is partly dissolved in the ferrite and partly associated with cementite; this makes the decomposition of the cementite more difficult, thereby opposing the softening action of the silicon. Graphite formation is accompanied by the evolution of heat, the effect being to slow up the cooling rate through the graphitisation range of temperature; thus, a low-carbon iron will cool more rapidly through this range than a high-carbon iron, which is one reason why the former are denser and sounder than the latter when cast with the same section thickness.

**Design of Sand Castings for Quantity Production.** N. F. Hindle. (*Metals and Alloys*, 1943, vol. 17, Apr., pp. 770–775; May, pp. 970–977; June, pp. 1196–1202). The preparation of sand moulds and the making of patterns and cores are discussed, and recommendations are made to assist the designer of castings with a view to meeting the foundryman's difficulties in the production of large quantities of castings in sand.

**Continuous Casting.** L. H. Day. (*Metal Treatment*, 1943, vol. 10, Winter Issue, pp. 233–238, 267). Supplementing a previous article (see p. 10 A) the author describes how finished and semi-finished strip and sheet can be produced straight from molten metal, eliminating the ingot and re-rolling stages. Details are given of the process developed in 1891 by the Fluid Metal Rolling Co., Maywood, Illinois; for this the plant consisted of a melting cupola, a converter, a Bessemer ladle, a tilting ladle, a Bessemer-type continuous casting machine and a Teplitz finishing train. The steel strip casting unit at the Crown Cork and Seal Co.'s works at Baltimore is also described.

**Outline Methods of Obtaining High Temperature Steel for Thin Sections.** H. H. Blosjo. (*American Foundryman*, 1943, vol. 5, Nov., pp. 2–4). An account is given of the melting practice at a steel foundry using a 1½-ton acid electric-arc furnace where it is necessary to tap the steel at a high temperature, because pouring of the thin-walled castings takes place at some distance from the furnace. As soon as a bath has formed under the electrodes, 30–40 lb. of slag from a previous heat are added. When the charge is first completely molten, the slag fracture should be black, and it should contain 30–35% of FeO. The manganese decreases until the carbon boil is quite pronounced. The carbon content begins to fall as the temperature increases, and this causes the FeO content of the slag to decrease. The colour of the slag fracture changes progressively from black, through grey and greenish-grey, to greenish-yellow. The carbon falls to 0·10–0·15% as the boil subsides, and the FeO in

the slag drops to 14–17%, the FeO + MnO content of the slag being 32–35%. To every ton in the melt 15 lb. of 80% ferro-manganese are added; this is preheated in a teapot ladle so as not to chill the bath. When the slag fracture is greenish-yellow and the carbon boil has practically subsided, a quick magnetic permeability test for carbon is made, and pig iron is added to raise the carbon to the desired level; the heat is tapped about 2 min. after this addition.

**Fundamentals of Core Making and the Selection of Proper Core Baking Equipment. Parts I., II. and III.** F. H. Faber. (*Industrial Heating*, 1942, vol. 9, Oct., pp. 1381–1384; 1943, vol. 10, Jan., pp. 84–90; Feb., pp. 242–250). The preparation of core sands and the properties of binders are discussed and several types of core-baking ovens are described.

**Heavy Castings in Green Sand.** H. Abnett. (*Institute of British Foundrymen: Foundry Trade Journal*, 1943, vol. 71, Dec. 30, pp. 353–354). A description is given of the method of preparing a green sand mould to cast a road roller wheel 6 ft. 6 in. in dia. in cast iron.

**Piston Rings of Gray Iron.** T. C. Jarrett. (*Metals and Alloys*, 1943, vol. 17, June, pp. 1188–1195). A brief description is given of American practice in the manufacture of grey iron piston rings. Illustrations of several stages of the process and micrographs of the structure of the metal are given.

## PRODUCTION OF STEEL

(Continued from pp. 79 A–82 A)

**The British Iron and Steel Industry.** (*Metallurgia*, 1943, vol. 29, Dec., pp. 73–75). A review is presented of what has been achieved by the British iron and steel industry since the outbreak of war in 1939. The problems which have been successfully overcome include: (1) The transport and use of far greater quantities of low-grade indigenous ores; (2) the conservation of alloying elements; (3) the reduction in the number of steel specifications; (4) black-out difficulties at steelworks; (5) the planning of factories for the mass production of cast steel bomb casings; and (6) the organisation of steel supplies and price stabilisation.

**The History of the Small Steelmaking Converter.** E. C. Pigott. (*Engineering*, 1943, vol. 156, Dec. 24, p. 515; Dec. 31, p. 535). A brief survey of the development of small converters for steelmaking is presented. The account begins with Bessemer's experiments, and is followed by details of many modifications in design, including that of Hatton, who, in 1883, patented a detachable bottom, and of the Walrand-Delattre converter with the tuyeres placed within 3 or 4 in. of the surface of the charge, at one side, and inclined at an

angle to give rotation to the bath. A process patented by Robert in Paris in 1889 brought the subject of the small converter into considerable prominence; after this came the Tropenas converter, which was introduced in 1891 and had reached a high degree of development by 1894. The Tropenas converter of to-day differs from the original in several respects. The upper row of tuyeres has now long been dispensed with in all plants, a shallower bath is provided, and both top and bottom sections are detachable.

**The Manufacture of Tool Steel in the United States.** H. Nathorst. (Iron and Steel Institute, 1943, Translation Series, No. 153). This is an English translation of a paper which appeared in Jernkontorets Annaler, 1941, vol. 125, No. 12, pp. 653-694. (See Journ. I. and S.I., 1943, No. 1, p. 51 A).

**A Study of a Shell-Steel Ingot.** D. Binnie. (Iron and Steel Institute, 1944, this Journal, Section I). An ingot of shell steel, teemed uphill and containing 0.47% of carbon and 0.88% of manganese, has been examined in some detail. Information is given on the manufacture of the steel. The sulphur print and analyses at the standard positions of the Committee on the Heterogeneity of Steel Ingots are shown. Longitudinal sections were cut from the feeder head and from the base of the ingot, and transverse sections from the top, middle and bottom of the ingot proper, all of which were subjected to close examination. The position of the chill equi-axed crystals, the columnar crystals and the equi-axed crystals behind the columnar crystals are illustrated; these areas have also been photographed after a copper etch, which brings out the dendritic structure. Among features brought to light is the presence of white spots of precipitated ferrite, seen in all sections of the ingot except the feeder head. The intensity and distribution of these white spots are considered. The lower half of the ingot had, on sulphur printing, a zoned effect: A light coloured zone at the surface, a dark zone, a light coloured zone and again the normal dark zone of the ingot. This zoning is compared with the acid-etched surface of the metal. A detailed analysis of the steel throughout the zoning is also given.

## FORGING, STAMPING AND DRAWING

(Continued from pp. 50 A-51 A)

**2500-Ton Six-Die Slide Press.** (Engineering, 1944, vol. 14, Jan. 14, pp. 27-28). An illustrated description is given of a six-station 2500-ton vertical hydraulic press which employs the rubber-pad technique; that is, instead of using a pair of solid-contoured dies, which must exactly match, only one die is required, the sheet metal to be shaped being pressed into, or over, the die contour by means of a rubber pad, which transmits the pressure applied to it in all directions instead of in one direction. The press has six columns

and six openings, through any of which the dies and material can be inserted and withdrawn. There is a central hydraulic ram, and the dies, which may be of a very different character, are assembled on rectangular die slides ; these slides, after loading, are run in under the press platen. Pressing can take place on one slide simultaneously with loading on the others.

**Evolution of a 1300-Ton Press.** R. H. Ferguson. (*Engineering Journal*, 1943, vol. 26, Nov., pp. 622-624). A description is given of the design of a 1300-ton hydraulic press with a 12-ft. gap capable of bending 1½-in. steel plate to make the shell plates of the drums of Yarrow boilers. The cylinder and ram of a 1000-ton horizontal press and two 190-ton rams from other machines were incorporated in the new vertical press. Details of the welded joints are given, for it was mainly due to the application of good welding technique that it was possible to construct the press from the limited material available.

**Forging Die Design.** J. Mueller. (*Heat Treating and Forging*, 1943, vol. 29, Sept., pp. 433-435). Some examples are given of the design of die blocks for 1200-lb. to 4000-lb. drop hammers.

**How to Design a Progressive Die.** C. W. Hinman. (*Heat Treating and Forging*, 1943, vol. 29, Oct., pp. 524-527, 536, 537). Recommendations are made for the design of a die for the production of circular brackets from  $\frac{5}{8}$ -in. steel strip, 1½ in. wide, in one stroke of the press at the rate of about 80 per min.

**Hard-Facing Hot Trimming Dies.** (*Machinist*, 1943, vol. 87, Dec. 25, pp. 98-100). A description is given of combination blanking and piercing punches and dies for trimming forged steel gate-valve disc rings. The edges of these dies are prepared by making a stellite deposit by oxy-acetylene welding on the carbon steel die blocks ; the deposit is then ground to the exact dimensions required. Dies made in this manner have given extremely good service.

**Improved Method Reduces Costs, Boosts Output 10 Times in Drawing Chromium-Molybdenum Steel.** I. H. Such. (*Steel*, 1943, vol. 113, Nov. 1, pp. 90-91, 124-126). A brief description is given of the pressing and drawing processes which have been developed for making light-weight cylinders for compressed gases for aircraft use out of chromium-molybdenum steel. These were formerly machined out of forgings, which meant a high percentage of scrap ; the amount of scrap has been reduced by 83%. The punches and dies are made of graphitic steels. About 40% of the total reduction is achieved in the first cupping operation, and the amount diminishes in subsequent stages. The cylinders are chemically cleaned after each draw and annealed at 1300° F. in a protective atmosphere. The final heat treatment consists of oil-quenching from 1550° F. and tempering at 1250° F.

**Tubular Railway Axles.** (*Steel*, 1943, vol. 113, Nov. 15, pp. 117, 162-164). Some particulars are given of the manufacture of tubular

railway wagon axles by the Pittsburgh Steel Co. In the piercing of the cylindrical billets, the rolls forming the tube are elliptical and rotate in a direction opposing the feed of the steel which is pressed against the rolls by a ram. After being cut to suitable lengths, the tubes are passed through a continuous furnace, which heats up one end of each tube; the heated ends are then upset in a press. The ends are subsequently shaped by a 3000-lb. drop hammer to form the wheel seats and journals. The processes of hardening, straightening and tempering follow. The finished axles have satisfactorily passed rigorous tests; their principal advantage is that they weigh from 25% to 43% less than the solid axles for equivalent rolling stock.

**Manufacture of Bayonets.** J. B. Nealey. (*Iron Age*, 1943, vol. 151, Mar. 4, pp. 62-66). A description is given of the sequence of processes in the manufacture of bayonets at an American factory. These processes include forging, trimming, annealing, machining, grinding, hardening, finish-grinding, assembly and inspection.

**Forging and Heat Treatment of Anti-Tank Shot.** (*Machinery*, 1943, vol. 63, Dec. 23, pp. 709-714). An illustrated description is given of the forging and heat-treatment processes applied in the manufacture of 37-mm. armour-piercing shot and cartridge cases.

**Mass Production of High Explosive Shells.** (*Machinery*, 1943, vol. 63, Dec. 30, pp. 729-734). A detailed and illustrated description is given of the processes developed at the Willys-Overland plant in the United States for the mass production of 155-mm. shells from  $5\frac{1}{2} \times 5\frac{1}{2} \times 15\frac{1}{2}$ -in. steel billets. The first piercing operation is done by a vertical hydraulic press and the cavity is then enlarged in a horizontal press. After checking for concentricity, the machining operations are carried out. An outstanding feature of the plant is the extensive use of conveyors, for there are 6300 ft. of overhead conveyors and 5000 ft. of the roller gravity type.

**Carbide Dies for Steel Shell Cases—Their Servicing.** E. Glen. (*Metals and Alloys*, 1943, vol. 17, Mar., pp. 536-538). The necessity for reconditioning carbide dies used in the drawing of steel cartridge cases before they are badly worn is stressed. In course of time a minute ring forms on the die surface where the front edge of the cartridge tube first makes contact with it. To dress the die a brass rod is placed in a hand grinder and, with No. 3 diamond powder as a grinding medium, this is brought to bear on the die, which is revolved in a lathe. The die is then polished with a felt wheel carrying No. 5 diamond powder.

**A Test for Measuring Drawability of Deep-Drawing Steels.** F. W. Boulger and F. B. Dahle. (*American Society for Testing Materials : Sheet Metal Industries*, 1943, vol. 18, Oct., pp. 1777-1780; Nov., pp. 1959-1966). The reasons for the failure of the present standard tests to evaluate the suitability of sheet metals for deep-drawing are discussed and an experimental test method is proposed in which flat circular blanks are drawn into round-bottomed cylindrical shells

by means of a simple die and plunger. This method utilises a cup-drawing procedure which takes account of all the properties required of a steel which has to withstand severe drawing operations. The data indicate that the cup-drawing method proposed is accurate and reproducible in showing differences between materials of ostensibly similar quality. A comparison of a few test results and service performance figures shows good correlation between breakages in the press and the cup-drawing ratings. The rating of the materials in the experimental test equipment according to their behaviour puts them in different order to that obtained by tensile, hardness and cupping tests. The data obtained indicate that increases in the carbon and sulphur contents lower the cup-drawing ratings, but that variations in manganese, copper and phosphorus over the ranges tested were without material effect. Temper-rolling the steel sheet lowered the cup-drawing ratings, the effect being most pronounced in the neighbourhood of 0·75% reduction.

**Die Reduction Charts.** (Wire Industry, 1943, vol. 10, Aug., pp. 345-353; Sept., pp. 399-405). A series of nine data charts is presented which gives the gauges of drawn wire, ranging in inlet size from 0·020 in. to 0·375 in. for all percentage reductions from a light rounding draft of 5% to a maximum roughing-down draft of 20%. The number of holes ranges up to 24. With these charts it is possible to ascertain immediately the drafting of any machine with any number of dies up to 24 at any specified reduction from 5% to 20%.

## HEAT TREATMENT

(Continued from pp. 84 A-89 A)

**The Treatment of Materials by the Deep-Freeze Process.** E. Gregory. (Machinery, 1944, vol. 64, Jan. 13, pp. 32-33). Some applications of cold treatment to steel and some non-ferrous metals are discussed. It has been generally accepted that room temperature is the final point in a heat-treatment process. It has been established by Gordon and Cohen, however, that the treatment at sub-zero temperature of 18/4/1 high-speed steel increases the Rockwell hardness and ductility with the result that the life of high-speed steel milling cutters can be considerably increased. Cold treatment also stabilises steel against changing in form or size. It was formerly necessary to "season" precision slip gauges for two years, but with cold treatment this period has been reduced to as low as two days. A unit for the cold-treatment of tools called the "Deep-freeze Cascade chilling machine" in which low temperatures are obtained in three stages, each requiring a suitable refrigerant, is described.

**Production of High Explosive Shells.** (Machinery, 1944, vol. 64, Jan. 13, pp. 35-39). The heat-treatment and machining operations

in the production of 155-mm. shells at the Willys-Overland plant are described and illustrated. The piercing and forging operations were described in an earlier article (*see p. 127 A*).

#### **Difficulties Encountered in the Heat Treatment of Drop Forgings.**

B. Thomas. (Staffordshire Iron and Steel Institute: *Metallurgia*, 1943, vol. 29, Nov., pp. 11-14). Some difficulties in the heat treatment of carbon and low-alloy steel drop forgings are discussed. The normalising temperature range recommended for steel En 8 is 830-860° C., but, as the carbon range for this steel is 0.30-0.45%, this temperature range is not wide enough, and failures in obtaining the minimum Izod value of 10 ft.-lb. occur. No alloy steel should ever be used without tempering after being quenched for hardening. For the higher-carbon nickel-chromium-molybdenum steels and nickel steels of the 4S11 and S69 types, tempering is usually necessary at between 600° and 650° C. The lower-carbon, but higher-chromium types, with nickel and molybdenum present (such as steel S65) are more frequently tempered at between 550° and 600° C., but the tempering temperature manganese-molybdenum steels may easily vary from 450° to 680° C.

**The Production Heat Treatment of Gears.** (Mechanical World, 1943, vol. 114, Nov. 19, pp. 583-586). The more important factors governing the classification and ultimate selection of steels for gears are discussed. The factors in favour of the lower-carbon case-hardening steels are cheapness, facility of heat treatment, good machining properties, toughness and high hardness after treatment. The disadvantages are marked distortion in all parts except those of the simplest design, the necessity of water-quenching, a tendency to form soft spots unless special quenching baths are made up, low core strength and sensitivity to tempering effects produced by friction in service. Alloy steels have greater hardenability by virtue of their lower critical cooling rate; this is a marked advantage for large sections. The application of full-hardening steels in gear manufacture is becoming increasingly popular. Another recent development is the use of cyanide baths for the heat treatment of full-hardening steels of the medium-carbon 1%-chromium type; the case depth obtained is of the order of 0.002-0.005 in., depending upon the mass of the part. Tables of the compositions of forged and rolled carbon and alloy steels for gears recommended by the American Standards Association, the American Gear Manufacturers' Association and the American Society of Mechanical Engineers are presented.

**"Three-in-One" Induction Heating Operation Simplifies Shaft Manufacture.** (Industrial Heating, 1943, vol. 10, Oct., pp. 1508-1510). **Induction Heating Saves Material and Forging Facilities.** (Heat Treating and Forging, 1943, vol. 29, Oct., pp. 539-540). A brief description is given of the application of induction heating to perform three operations simultaneously on Diesel engine shafts, namely, to harden a bearing surface and a thrust face, and to braze a collar on the shaft.

**The Annealing of Steel.** P. Payson. (*Iron Age*, 1943, vol. 151, June 24, pp. 44-47, 130; vol. 152, July 1, pp. 48-54; July 8, pp. 74-77; July 15, pp. 70-77; July 22, pp. 60-67). In this series of articles the author refers to various definitions of annealing and discusses the following rules for carrying out the process : (1) The higher the austenitising temperature, the greater is the tendency for the structure of the annealed steel to be lamellar, whereas the closer the austenitising temperature is to the critical temperature, the greater the tendency for the structure of the annealed steel to be spheroidal ; (2) to develop the softest condition austenitise at somewhat less than 100° F. above the critical point and transform at rather less than 100° F. below the critical point ; (3) as the time for complete transformation at less than 100° F. below the critical point may be very long, allow most of the transformation to take place at the higher temperature at which a soft product is formed and finish the transformation at a lower temperature where the time for completion is short ; (4) after austenitising, cool the steel as rapidly as possible to the transformation temperature and, after complete transformation, cool to room temperature as rapidly as possible so as to cut down the total annealing time ; (5) to ensure a minimum of lamellar pearlite in the structure of annealed high-carbon tool steel (carbon 0.70-0.90%), and low-alloy medium-carbon steels, preheat the steel for several hours at about 50° F. below the critical point before austenitising ; and (6) to obtain minimum hardness in annealed hypereutectoid alloy tool steels, heat the steel 10 to 15 hr. at the austenitising temperature and transform as usual. Transformation-time/temperature curves for a wide variety of steels are presented and discussed.

**Centrifugal Quenching Machine.** (*Engineering*, 1944, vol. 157, Jan. 7, p. 7). An illustrated description is given of the Hannifin quenching machine for quenching circular parts such as gear and sprocket wheels, flat cams, bearing rings, &c. In this machine, the principle of quenching the heated circular part from the periphery towards the centre is applied, and all parts of the periphery are immersed in the cooling oil at the same time. The quenching chamber contains adjustable supports on which the rim of the wheel to be hardened rests and rams can be made to exert pressure on the wheel centre from above or below to correct any distortion. The chamber is spun on a vertical axis, and the cooling oil enters it over a deflector plate which directs it to the chamber wall ; centrifugal force causes the oil to build up with a vertical surface, and this surface approaches and passes over the periphery of the wheel as more oil is pumped into the chamber. The quenching time, the volume of the quenching medium and its temperature can all be controlled.

**New Handling Method Devised for Speeding Transfer of forgings from Furnace to Quenching Tank.** (*Industrial Heating*, 1943, vol. 10, Oct., pp. 1500, 1504). A means for rapidly transferring large

forged steel rings from the heat-treatment furnace to the quenching tank is described and illustrated. A pair of hooks, specially designed to grip under the bottom edge of the ring, is suspended from a crane over the track just outside the furnace door; these hooks are held apart by operators standing on each side of the track. The car carrying the forging is pulled out of the furnace, and the two hooks are allowed to swing in under the forging; the crane lifts the latter off the car, travels with it to the quenching tank, which is below floor level 15 ft. to one side of the track, and lowers it into the oil, the whole operation taking 25 sec. from the time of opening the furnace doors.

## WELDING AND CUTTING

(Continued from pp. 90 A-92 A)

**The Weldability of Cast Iron.** T. J. Palmer. (*Metallurgia*, 1943, vol. 29, Nov., pp. 3-6, 25; Dec., pp. 97-100). The different types of cast iron are outlined and certain microstructural differences in them are illustrated. The oxy-acetylene welding of cast iron and the precautions to take to prevent cracks and porosity and to ensure a machinable deposit are discussed. In the preheating, the range 650-750° C. should be reached gradually; the weld should be made rapidly and the part cooled slowly. For low-temperature welding, preheating to 400-450° C. is sufficient in most cases; the filler rod is a close-grained special alloy cast iron containing a little nickel. A flux paste is applied to the work after it has been lightly heated. A torch of normal power is held at a fairly flat angle to the work, and the metal is raised locally to a bright red heat (about 850° C.); the end of the rod is then melted, when it should spread out and effectively cover the area directly under the torch flame. Stirring or puddling with the rod is not required with this welding as the parent metal is not melted.

**Welded and Riveted Joints Compared.** J. Dearden. (*Metal Treatment*, 1943, vol. 10, Winter Issue, pp. 207-210, 232). The resistance of welded and of riveted joints to static and dynamic loading is compared with that of the as-rolled parent plate, and some of the literature on the strength of welded joints is reviewed. The principal lesson to be learned from a study of the published results of fatigue tests on welded joints of all kinds is that surface finish of the joint is of paramount importance. When riveting and welding are combined in a joint, it is more than likely that before the necessary movement to distribute the load within the riveted portion can occur, the whole of the load will have been taken up by the welded portion. Some authorities consider that it is possible to increase the total strength of the joint if the welding reinforcement is applied while the riveted joint is under load.

**Spot Welding of S.A.E. 1020, 1035 and 1045 Steels in the 0-040 In. Thickness.** W. F. Hess and D. C. Herrschaft. (Welding Journal, 1943, vol. 22, Oct., pp. 451-S-461-S). A report is presented on the development of the optimum welding conditions for the spot welding and tempering in the welding machine of three plain carbon steels (carbon 0·20%, 0·35% and 0·45%, respectively). Remarkable improvements in the physical properties were obtained by the tempering in all three cases, the greatest effect being noted with the steel of highest carbon content. Even in the steel lowest in carbon the tensile strength measured perpendicular to the surface of the sheet was tripled by the tempering treatment; with the 0·45% carbon steel this value was increased ten times. The tempering of spot welds in thin gauges of hardenable steels in the welding machine was shown to be both beneficial and entirely practicable.

**Electric Resistance-Welded Steel Tubing—Its Quality Control and Application.** R. D. Malm. (Welding Journal, 1943, vol. 22, Oct., pp. 818-821). A process of making tubing from steel strip is described. Strip is fed from a coil into a conventional multiple-stand cold-forming mill, which bends it progressively and continuously into cylindrical form with an open seam; this cylinder is forced beneath a pair of roller electrodes which make contact one on each side of the seam close to the edges. When the edges make contact the resistance to the heavy current brings the steel up to welding heat; mechanical pressure is applied to force the edges together. Some metal is extruded on the inside and outside surfaces, and this is removed while the metal is still hot. The tubes are afterwards heat-treated and tested.

**Welded Steel Tubes for Maximum Torsional Resistance.** W. J. Conley. (Steel, 1943, vol. 113, Nov. 22, pp. 82, 90). Examples are given of the design of welded joints between tubular steel members.

**The Effect of Normalizing on the Properties of Welds in Carbon-Molybdenum Steel Pipe.** I. A. Rohrig, D. H. Corey and S. Crocker. (Welding Journal, 1943, vol. 22, Oct., pp. 521-S-527-S). The results of a laboratory investigation to determine the effect of normalising arc-welded joints in carbon-molybdenum steel tubes instead of stress-relieving them at 1150-1250° F. is described. The conclusions reached were: (1) Normalising carbon-molybdenum weld metal at 1550°, 1650° and 1725° F. for 1 hr. has no significant effect upon its tensile strength, which in all cases remains above 60,000 lb. per sq. in.; (2) the notched-bar impact strength of carbon-molybdenum steel weld metal is improved by normalising at 1725° F.; (3) the toughness of hot-rolled carbon-molybdenum steel tube metal is improved by normalising at 1725° F.; (4) the toughness of the heat-affected zone near the weld is good in the as-welded condition and is not greatly affected by normalising at 1725° F.; (5) the heat-affected zone can be made to disappear by normalising at 1550° F., but after such heat treatment the grain size of the tube metal is finer than desired; (6) the grain structure of

carbon-molybdenum steel weld metal is improved by normalising at up to 1900° F.; at 1725° F. the Widmanstätten areas become evident, but very little grain growth occurs; and (7) carbon-molybdenum weld metal has no grain-coarsening tendency at up to about 1800° F.

**Stored Energy Welding of Mild Steel.** J. M. Diebold. (Welding Journal, 1943, vol. 22, Oct., pp. 484-S-493-S). The results of tests on the strength of spot welds in mild steel sheet, made with a condenser-discharge welding machine, are presented. Curves are reproduced which relate the strength of the welds to the discharge voltage for different gauges of sheet and different mechanical pressures on the electrodes. This stored-energy method of welding was found to be excellent for light gauges of mild steel. Very uniform results were obtained, and, with the correct capacitor settings, the flashing and spatter were so little that the metal finishing costs could be considerably reduced.

**A Possible Application of Ultrasonics.** A. Behr. (Metal Industry, 1943, vol. 63, Dec. 31, p. 422). Earlier work on the effect of supersonics on the solidification of molten metals is briefly reviewed, and the suggestion is made that the conditions encountered in welding are most suitable for the application of supersonics to refine the grain and improve the properties of the weld metal. The volume of molten and solidifying metal which would have to be exposed to the action of supersonic vibrations at any one time is quite small, also, as the parts to be welded together are solids, they constitute the best possible conductors of supersonic vibrations and the most suitable means of conveying these vibrations to the molten and solidifying weld metal. The most promising field of application would undoubtedly be spot welding. By passing a beam of supersonic vibrations into the region of the spot weld during and after its formation, the cast structure of the weld nugget or "slug" could be effectively broken up and the mechanical properties of the spot weld appreciably increased.

**Establishment of Cooling Curves of Welds by Means of Electrical Analogy.** V. Paschkis. (Welding Journal, 1943, vol. 22, Oct., pp. 462-S-483-S). A preliminary investigation to throw light on the mechanism of heat flow during the cooling period in the arc welding of steel plates is reported. It is planned to set up complete cooling curves for many combinations of conditions, such as plate thickness, position of weld, energy input and preheating temperature. The present experiments were limited to the top pass on steel plates  $1\frac{1}{2}$  in. thick. The investigations were carried out by the "method of electrical analogy," using the equipment at Columbia University known as the "heat and mass flow analyser." The theory of the method has been explained previously (see Journ. I. and S.I., 1942, No. I., p. 133 A), and its particular application in the present problem is described in detail in an appendix. General cooling curves showing the different cooling rates at different positions in a  $1\frac{1}{2}$ -in.

plate for various rates of energy input, welding speeds and preheat temperatures are presented, and from these, two general charts, one for energy transfer by radiation and the other for the heat transferred in the metal melting off the electrode, are constructed.

**Weld-Bead Hardness Tests on Some Carbon, Nickel and Nickel-Chromium War Department Steels.** O. E. Harder and C. B. Voldrich. (*Welding Journal*, 1943, vol. 22, Oct., pp. 441-S-450-S). A report is presented of the apparatus and procedure for making Vickers hardness tests on weld beads on  $6 \times 3 \times \frac{1}{2}$ -in. specimens representative of 34 plain carbon, nickel and nickel-chromium steels supplied to Watertown Arsenal. The test data are given in numerous tables and graphs. The maximum hardness developed in the heat-affected zone is related to the carbon content plus one-sixth of the manganese content. For the steels studied, lowering the plate temperature from  $65^\circ$  to  $-20^\circ$  F. had little or no effect on the maximum hardness and in no case caused cracking, but raising the plate temperature from  $65^\circ$  to  $300^\circ$  F. lowered the maximum hardness considerably and eliminated cracks in five out of six of the steels which developed cracks when the plate temperature was  $65^\circ$  F. Under the testing conditions used, a specification limiting the maximum hardness in the heat-affected zone appears to be much more severe than one specifying freedom from cracks, because the minimum hardness at which a crack was found was 566 on the Vickers scale.

**Machine Cutting for Assembly Line Fabrication.** C. O. Adams. (*Welding Journal*, 1943, vol. 22, Oct., pp. 776-779). An account is given of the part played by oxy-acetylene cutting machines in a fabrication assembly line set up for making large numbers of Diesel-electric generators. Some machines were set up for repetitive shape cutting of both large and small parts, as well as for partially fabricated units; other machines with multiple burners set at different angles were used to prepare plate edges for welding.

## PROPERTIES AND TESTS

(Continued from pp. 100 A-107 A)

**An Investigation of Different Methods of Testing Cast Iron.** G. Meyersberg. (*Teknisk Tidskrift*, 1943, vol. 73, Dec. 11, pp. B99-B108). (In Swedish). The author reports the results of bend, tensile, shear, torsion and hardness tests on cast iron in which the data obtained in four German, one French and four Belgian laboratories are compared. Eleven different types of iron were prepared, and twelve round and twelve square specimens, 760 mm. long, of each type were cast for each of the nine laboratories. The mean values and the scatter of each series of test results are presented in

tables and graphs. There was no appreciable difference in the bend test results by the Belgian and German methods. In the tensile tests a mean spread of 3·7% was obtained when the standardised conditions were properly maintained. When the Brinell tests were carefully made a scatter of less than 2% was obtained.

**The Influence of Carbide Formers on the Yield Point of Steel at Room Temperature.** K. Dies. (Iron and Steel Institute, 1944, Translation Series, No. 173). An English translation is presented of a paper which appeared in Archiv für das Eisenhüttenwesen, 1943, vol. 16, Mar., pp. 333–339 (see Journ. I. and S.I., 1943, No. II., p. 126 A).

**The Metallurgy of Modern Alloys.** R. H. Harrington. (Heat Treating and Forging, 1943, vol. 29, Oct., pp. 515–518). Continuation of a series of articles (see Journ. I. and S.I., 1943, No. II., p. 202 A). In Part III. the terms "strain," "elastic strain" and "plastic strain" are defined. In Part IIIA. the rôle of strain in reactions of the solid state relative to plastic deformation and recrystallisation in non-ferrous alloys is discussed.

**Cracks in Wheel Seats within the Hubs of Wheels.** G. W. C. Hirst. (Engineering, 1943, vol. 156, Dec. 24, pp. 501–502). Test data and theories concerning the distribution of stresses in the axles of locomotives and wagons on which wheels are press-fitted are discussed. A photo-elastic representation of the case in which radial pressure from the hub is combined with a bending moment is reproduced. In an earlier mathematical analysis by the present author it was assumed that the radial pressure upon the whole of the wheel seat within the hub was uniform and it was shown that such a pressure causes a tensile stress of half the magnitude of the radial pressure from the hub in the surface of the axle and just outside the hub. In the surface of the axle and within the hub, the stress is compressive and tends to prevent the formation of cracks in this locality. A series of investigations on a model depicting the effect of press fit only confirmed the mathematical analysis. A new analysis of the photo-elastic stress diagram presented is made and it is shown that if there are local concentrations of compressive stress on the compressed side of the axle, the effect of the press fit is to increase the range of stress and make the axle appear weaker than is expected. If there are no local concentrations of compressive stress on the compressive side of the axle, the mean stress of the alternating stresses is tensile; this also makes the axle weaker than would be expected. In either case the tensile stress is of paramount importance.

**The Micro-Hardness Tester—A New Tool in Powder Metallurgy.** R. Steinitz. (Metals and Alloys, 1943, vol. 17, June, pp. 1183–1187). A description is given of a new micro-hardness testing instrument. It carries a diamond penetrator mounted so that it can be attached to a microscope in place of the object lens. The microscope has cross hairs in the eye-piece, and by properly aligning the diamond, it can be made to touch the sample under investigation on the exact

spot previously indicated by the cross hairs. The diamond is lowered on to the sample by turning the fine-adjustment screw of the microscope. The force applied soon becomes sufficient to overcome that of a carefully calibrated spring; when this occurs two contacts held by the spring are opened, a small lamp is illuminated and the penetrator is raised; this ensures that the same force is always applied. Some micrographs are presented of the indentations obtained in particles of iron powder, sponge iron and sintered compacts.

**Alloy and Special Steels.** J. W. Donaldson. (*Metallurgia*, 1943, vol. 29, Dec., pp. 75-78). A review is presented of the properties and compositions of some of the alloy steels which were developed prior to the outbreak of war in 1939 and information is given on some of their war-time applications.

**Gun Steels.** A. E. W. Smith. (*Journal of the Royal Artillery*, 1944, vol. 71, Jan., pp. 17-24). A brief account is given of the development of steels for gun barrels with reasons for the necessity of using heat-treated nickel-chromium-molybdenum steel to withstand the heat and shock to which modern heavy guns are subjected on firing.

**Chromium-Manganese "Stainless" Irons.** J. M. Parks. (*Metals and Alloys*, 1943, vol. 17, Feb., pp. 330-335; Mar., pp. 539-543). The microstructure and properties of chromium-manganese-iron alloys have been investigated using rods hot-rolled and forged from 2-kg. ingots prepared in a small induction furnace. The irons contained 12%, 20% and 30% of manganese with 12% of chromium, and 12% and 20% of manganese with 5% of chromium. The structure of these chromium-manganese irons is duplex and consists of austenite and ferrite, or austenite and the  $\sigma$ -phase, depending upon the composition and heat treatment. The influence of the manganese is to reduce the amount of rejected ferrite; the chromium has little effect on the amount of ferrite rejected. Water-quenching and furnace-cooling have little influence on the hardness, although the decomposition of the ferrite into the  $\sigma$ -phase is encouraged by the slower cooling. The irons studied have little resistance to the attack of sulphuric acid and hydrochloric acid, although they have fair resistance to nitric acid. When the lower-manganese irons are cold-reduced, the increase in hardness is greater than that for the higher-manganese irons. Generally speaking, the 12%-chromium irons can be worked to about 60% reduction in area before failure occurs due to overworking; in this working process an ultimate strength of over 200,000 lb. per sq. in. may be attained. The 5%-chromium irons do not attain this strength on cold-working. The chromium-manganese irons have equal, if not better, ultimate strength in the annealed condition compared with the chromium-nickel steels in the same condition.

**User Report No. 22 on Experience with NE (National Emergency) Alloy Steels.** G. Bissett. (*Steel*, 1943, vol. 113, Nov. 15, pp. 132-

135, 170). Some examples are given of the successful replacement of S.A.E. steels for aircraft parts by some of the 8000 and 9000 series of National Emergency steels.

## METALLOGRAPHY AND CONSTITUTION

(Continued from pp. 107 A-109 A)

**The Electron Microscope and Its Application to Engineering Problems.** A. G. Quarrell. (*Engineer*, 1943, vol. 176, Dec. 24, pp. 499-502; Dec. 31, pp. 526-528). The principles, development and application of the electron microscope are discussed. The pioneer work on the high-resolution electron microscope was carried out by Knoll and Ruska in 1932. The type of instrument in use in the United States is described. Unit construction is adopted throughout, the electron tube unit, condenser coil and object chamber unit being joined together by plain ground surfaces sealed with low-vapour-pressure grease to give vacuum-tight joints. The flexibility necessary to enable these joints to be kept tight while the different units are adjusted is obtained by means of metallic bellows incorporated in the vacuum line. Methods of obtaining and supporting replicas of metallographic specimens are described and electron micrographs of zinc oxide smoke, pearlite, a silver halide crystal and annealed brass are reproduced. In addition to the above type of electron microscope, other electron-optical microscopes classified by L. C. Martin as cathode, simple electron and field emission microscopes are discussed and the literature on them reviewed.

**Identification of Non-Metallic Inclusions in Steel.** C. A. E. Wilkins. (*Metal Treatment*, 1943, vol. 10, Winter Issue, pp. 211-224). Five methods of identifying and studying non-metallic inclusions in steel are described; these are: (1) Ordinary microscopic examination; (2) reflected polarised light; (3) etching with various reagents; (4) heat tinting; and (5) chemical analysis. Sixteen micrographs of different types of inclusions classified by the author's method are reproduced and the literature on other methods of identification is reviewed.

**Radiography Aids Steel Casting Technique.** G. W. McCleary. (*Canadian Metals and Metallurgical Industries*, 1943, vol. 6, Nov., pp. 23-26). A description is given of the gamma-radiography technique employed at a Canadian foundry to detect faults in steel castings. The gates and risers were removed the day after casting; this was followed by sand-blasting. They were then arranged in a circle of about 5 ft. dia. with the radium capsule on a stand in the centre and the sensitive plates were set up behind the castings; slow plates were used for an over-night exposure of 15 hr. These were developed next morning and it was thus possible to detect porosity

and blow holes and to correct the casting technique within 48 hr. of pouring the first castings. To be able to test them in the as-cast instead of the finish-machined state also contributed to the saving of time and expense. Several radiographs of castings are reproduced.

**X-Ray Crystallography as a Routine Operation.** (Iron and Steel, 1943, vol. 17, Dec., pp. 190-191). A description is given of the X-ray equipment developed by Metropolitan-Vickers Electrical Co., Ltd., for routine crystallographic analysis. This apparatus is particularly robust and simple, though quite flexible in its application. It incorporates two types of camera, known respectively as the "powder" and the "universal." Highly skilled operators are not required, as persons of ordinary intelligence can carry out many kinds of crystallographic analyses as a routine, quickly and surely without any specialised training.

**The Interpretation of the Crystal Structure of Cementite.** N. J. Petch. (Iron and Steel Institute, 1944, this Journal, Section I). Previous work on the structure of cementite with which the author was associated is extended. The nature of the valency forces in the structure is considered, and it is suggested that cementite is essentially a framework of close-packed iron atoms held together by metallic bonding, with the small carbon atoms in the largest interstices, these atoms also being held in position by bonding which has a certain degree of metallic nature. This implies a close general resemblance to ferrite and austenite, and suggests that cementite may have many characteristics of a solid solution. The possibility of variation in the cementite composition is considered, and experimental work on this point is described. Lattice-parameter variations are observed which appear to indicate composition variation. The interpretation of the cementite structure is illustrated by applying it to the question of the influence of alloying elements on graphitisation.

**The Nature of Pure Metals.** J. F. Young. (Mechanical Engineering, 1943, vol. 65, Nov., pp. 795-801). Some fundamental concepts relating to pure metals are defined and explanations of lattice structure, allotropic change, grain growth, the object of etching, grain structure in castings, hot and cold working, plastic deformation, preferred orientation and recrystallisation are given.

## CORROSION OF IRON AND STEEL

(Continued from pp. 109 A-111 A)

**Corrosion of Tin-Nickel Alloy Coatings on Steel in Canned Food-stuffs.** H. R. Copson and W. A. Wesley. (Electrochemical Society, Oct., 1943, Preprint No. 84-23). An account is given of electrolytic corrosion tests under anaerobic conditions to determine the corrosion resistance of steel sheet coated with nickel and tin. The steel was

plated with equal thicknesses of nickel and then tin, and was then heated for 6-8 min. at 300° C.; this left a nickel-rich layer next to the steel and a tin-rich layer on top, with a diffusion zone in between having a composition corresponding closely to  $\text{Ni}_3\text{Sn}_4$ . The tests consisted of running four galvanic couples in each of five foodstuffs (prunes in syrup, sauerkraut, tomatoes, spinach and peas) in sealed pyrex glass jars held at 100° F. for periods up to 256 days. Measurements of potential, current, loss in weight and pitting depth were made. Two of each set of four couples consisted of steel and nickel-plus-tin coated steel, the third of steel and tinplate, and the fourth of steel and nickel. The results indicated that the nickel-plus-tin coatings were anodic to bare steel in all the foods except spinach. This indication, together with observations of the degree of corrosion, lead to the conclusion that nickel-plus-tin coatings would make a satisfactory substitute for heavier coatings of tin only.

**First Report on Stress Corrosion Cracking of Stainless Steel in Chloride Solutions.** M. A. Scheil, O. Zmeskal, J. Waber and F. Stockhausen. (Welding Journal, 1943, vol. 22, Oct., pp. 493-S-506-S). An account is given of the preliminary study to find suitable solutions to use in an investigation, at the Illinois Institute of Technology, of the transgranular cracking of stainless steel under stress-corrosion conditions. Austenitic 18/8 steels and ferritic chromium steels were used. The specimens were  $8 \times \frac{1}{2} \times \frac{1}{8}$  in. with a hole drilled in each end; the two ends were bent over to form a wide channel and a predetermined stress was applied to the bent arms which were then locked in position by passing a bar through the holes and screwing up a nut at each end. The specimens, stressed in this manner, were immersed in different solutions for periods of up to 500 hr. and examined. None of the ferritic chromium steels cracked in boiling 50% magnesium-chloride solution; the austenitic steels all exhibited cracks. In boiling 40% magnesium-chloride solution acidified to pH4 with either hydrochloric acid, or with acetic acid and sodium acetate, the results were very similar, none of the ferritic chromium steels exhibiting cracks and all the austenitic steels failing in a short time; the latter solution caused a green scale to form, but the former was considered suitable for more extensive tests. Mixtures of magnesium-chloride and calcium-chloride solutions gave sporadic results; boiling saturated barium-chloride solution acidified with hydrochloric acid and boiling 10% calcium chloride solution acidified with nitric acid did not produce any cracks.

**The Corrosion of Mains in Clay Soils.** H. J. Bunker. (Institution of Sanitary Engineers : Industrial Heating Engineer, 1944, vol. 6, Jan., pp. 8-10). The rapid corrosion of cast-iron water mains in clay soils is discussed. It is often found that the soil near the pipe is black, and in severe cases it is possible to detect the unpleasant odour of sulphuretted hydrogen as the burst on a corroded length is laid bare. The true explanation of this corrosion is of a biological nature

for it is due to sulphate-reducing bacteria called *Vibro desulphuricans*. These are very wide-spread in nature and flourish under anaerobic conditions. In clay soils containing sulphates, by reducing these sulphates to sulphide, the bacteria render the sulphate available to act as an acceptor for the hydrogen, and thus fulfil the function of preventing polarisation at the cathodic points, so that corrosion is able to proceed. At the same time, the hydrogen sulphide resulting from the reduction of sulphates combines with the iron ions going into solution at the anodic points, with the consequent deposition of iron sulphide.

## ANALYSIS

(Continued from pp. 71 A-73 A)

**Advances in Micro-Chemistry II.—Micro-Analytical Methods of Examining Iron and Steel.** P. Klinger, W. Koch and G. Blaszczyk. (Iron and Steel Institute, 1943, Translation Series, No. 169). This is an English translation of a paper which appeared in Angewandte Chemie, 1940, vol. 53, Nov. 23, pp. 537-549, and in Technische Mitteilungen Krupp, Forschungsberichte, 1940, vol. 3, p. 255 *et seq.* After an introduction, in which the latest developments of micro-analysis are outlined and the cases discussed in which its application to the examination of metals is advantageous, detailed information is given on the methods adopted for micro-analytical determinations of iron, carbon, silicon, manganese, phosphorus, sulphur, aluminium, nitrogen, chromium, nickel, molybdenum, tungsten, titanium and vanadium in ferrous alloys. The methods involve gravimetric, volumetric, colorimetric, electrolytic and polarographic determinations. The results obtained for the various elements are listed in tables, showing also the sample weights required and the accuracy attainable in comparison with macro-methods. In conclusion some procedures are described which permit of the micro-determination of several elements in one alloy sample.

**Metallurgical Microchemistry.** E. C. Pigott. (Metal Treatment, 1943, vol. 10, Winter Issue, pp. 239-248, 272). The advantages of microchemical analyses are discussed and illustrated descriptions of the Bolton and Williams photo-electric colorimeter, the Spekker photo-electric absorptiometer, the Klett-Summerson photo-electric colorimeter and the Cambridge polarograph are given.

**The Determination of the Aluminium Content of Steel.** E. Hammarberg and G. Phragmén. (Jernkontorets Annaler, 1943, vol. 127, No. 12, pp. 608-622). (In Swedish). Methods given in the literature for the determination of aluminium in steel are reviewed and those which give accurate results without being too tedious are more critically examined. A method for unalloyed and

low-alloy steels is described in detail. In this, most of the iron and some of the other elements are removed by electrolysis using a mercury cathode. The aluminium is separated from the manganese by precipitation of the former as phosphate from a weak acid solution. Traces of iron, titanium and vanadium are precipitated with cupferron solution. After evaporation with perchloric acid to fumes (but without the formation of solid salts) to destroy the excess of cupferron, which also oxides the chromium to chromic acid, the diluted solution is filtered to remove silica. The aluminium is then precipitated as aluminium phosphate which is ignited and weighed. Good agreement was obtained between results by this method and by a spectrographic method even with as little as 0·001% of aluminium present.

**The Determination of Phosphorus in Iron and Steel by Means of the Spekker Photo-Electric Absorptiometer. An "Arsenic-Free" Method.** T. S. Harrison and W. Fisher. (*Journal of the Society of Chemical Industry*, 1943, vol. 62, Dec., pp. 219-221). Phosphorus may be determined in iron and steel by means of the Spekker photo-electric absorptiometer. The method described gives reliable and reproducible results, and is quicker than any of the usual chemical processes. Important factors which contribute to its success are the removal of any arsenic present, and the employment of the stable phospho-vanado-molybdate complex for absorptiometric measurement.

**Determination of Tungsten in Low-Grade Tungsten Ores.** F. S. Grimaldi and V. North (*Industrial and Engineering Chemistry, Analytical Edition*, 1943, vol. 15, Oct., pp. 652-654). Two methods based on the Feigl-Krumholz test are described for the rapid colorimetric determination of very small amounts of tungsten in low grade ores and tailings.

**The Determination of Molybdenum and Tungsten in Ores by Spectrum Analysis.** C. G. Carlsson. (*Jernkontorets Annaler*, 1943, vol. 127, No. 11, pp. 572-582). (In Swedish). A method of determining small amounts of molybdenum and tungsten (from 0·01% to 0·5% of  $\text{MoS}_2$  and  $\text{WO}_3$ ) in ores by spectrum analysis is described. A copper electrode 20 mm. long and 3 mm. in dia. is prepared by drilling a hole 2·6 mm. in dia. and 2 mm. deep in the centre of one end; the hole is filled with the finely ground sample, mixed with ferrous oxide and a potassium salt. A direct-current arc is used. In the 0·01-0·25% range the results are accurate to within  $\pm 0\cdot01\%$ . The first two determinations in one sample take 1 hr. and subsequent determinations can be made in 30 min.

**An Improved Electrode Holder for Spectrographic Analysis.** B. F. Scribner and C. H. Corliss. (*Journal of Research of the National Bureau of Standards*, 1943, vol. 30, Jan., pp. 41-45). A detailed description is given of an electrode holder for facilitating operations in miscellaneous spectrographic testing. The advantages of this holder include : (1) It can be applied to a variety of electrode sizes

and excitation conditions ; (2) positive and precise adjustment and motion of the parts can be obtained ; (3) water-cooling of the clamps is provided ; and (4) a housing is fitted for protecting the operator against light, fumes and shock.

**Electrographic Analysis.** D. L. Masters. (*Metallurgia*, 1943, vol. 29, Dec., pp. 101-104). A description is given of the electrographic method of analysis and some special applications of it. In a simple form of apparatus a base plate of insulating material is covered with a sheet of aluminium which forms the cathode ; on this is laid a sheet of absorbent paper moistened with a suitable electrolyte such as potassium chloride or potassium sulphate solution ; another sheet of absorbent paper carrying the reagent or reagents is put on this. Finally the specimen is placed on top face downwards and the pack is pressed together by a plate on top of the specimen which is the anode. The current is supplied by a small battery of dry cells. Ions are thus transferred from the specimen and are detected by the colours they give with the reagent in the absorbent paper. Examples of the application of this technique include the detection of porosity in chromium plating on top of nickel-plated steel ; minerals containing copper, nickel and cobalt have been investigated by a single test.

## MINERAL RESOURCES

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(Continued from p. 37 A)

**Ores as the Foundation for Sweden's Iron Production and Swedish Ore Exports.** K. Rutberg. (*Jernkontorets Annaler*, 1943, vol. 127, No. 12, pp. 585-607). (In Swedish). Statistics are presented of the production and concentration of Swedish iron ores, the imports of coal and coke, the production of pig iron and steel, the exports of ore, number of men employed and some of the costs. For most of the items the data are for the period 1922-1939. Calculations are made relative to the ore-beds in central Sweden covering an area of about 400,000 sq. m., which show that the ore over this area contains about 465,000 metric tons of iron per metre depth. In 1939 the iron content of the ores exported from central Sweden exceeded 1.5 million tons, which is equivalent to the removal of ore from that ore-bearing area to an average depth of between 3 and 4 m.

**Outlook for Iron from Brazil.** F. G. Pardee. (*Engineering and Mining Journal*, 1943, vol. 144, Oct., pp. 75-77). The iron ore resources of the Minas Geraes region in Brazil are reviewed. The reserves in this State have been estimated at 15 billion tons (a U.S. billion =  $10^9$ ), of which 1 billion tons is assigned to the Itabira deposits. The total is made up of  $1\frac{1}{2}$  billion tons of compact hematite with about 65% of iron,  $3\frac{1}{2}$  billion tons with 50-60% of iron and 10 billion tons with 30-50% of iron. The situation of the ore in relation to the existing railways is discussed.

## FUEL

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(Continued from pp. 75 A-77 A)

**Hand-Fired Furnaces.** D. J. Bradbury. (*Iron and Steel*, 1944, vol. 17, Jan., pp. 238-240). Some common sources of heat loss in hand-fired furnaces are described. They are of a rather obvious nature, but experience has shown them to be frequently overlooked. Included among them are badly spaced firebars, unsatisfactory draught control, no provision for secondary air supply, badly fitting doors, neglected brickwork and inefficient steam injection.

**A Question of Nomenclature.** J. Roberts. (*Coke and Smokeless-Fuel Age*, 1944, vol. 6, Jan., pp. 9-10). The meanings of the terms "coke," "coking," "non-coking," "char" and "caking" are discussed. A non-coking coal is one which, on baking, yields a residue which is non-coherent, unfused and possesses no cellular coke structure. When such a coal is carbonised without being

crushed it can be made to yield a desirable smokeless fuel called "char." The process of manufacture is called "charring" rather than "coking," but the term "carbonisation" can be used to embrace the production of both char and coke. Some writers describe coals which will yield satisfactory cokes in retorts or coke-ovens as "coking" coals, and coals of poor fusibility which could not be baked alone as "caking" coals, but the author considers that the term "caking" should not be used at all and prefers to call the latter type of coal a "weakly coking coal" or a "poor quality coking coal."

**Modern Beehive Coke-Oven Practice.** G. S. Scott, J. A. Kelley, E. L. Fish and L. D. Schmidt. (United States Bureau of Mines, Dec., 1943, Report of Investigations No. 3738). To make up the shortage of coke required for blast-furnaces in the United States, many batteries of beehive ovens are now in operation. In some cases the coke produced is of poor quality. In order to investigate the causes of this, a travelling laboratory was fitted out to tour the Pennsylvania beehive coke-making district. Tests were first conducted at a battery making good-quality coke, and the present paper presents the results obtained and includes screen analyses of the raw coal, gas analyses and temperature readings. During the first 20 hr. the rate of evolution of volatile matter was roughly proportional to the rate of flow of air through the oven. After this period the rate of volatilisation began to decline, and continued to decline during the rest of the coking period. Details of the gas-analysis procedure are given.

**Tests of the Heliopore Coal-Carbonization Power-Plant Process.** A. C. Fieldner, J. D. Davis, V. F. Parry, L. D. Schmidt, J. L. Elder, J. B. Goodman, W. S. Landers and E. W. Goodwin. (United States Bureau of Mines, Dec., 1943, Report of Investigations No. 3733). A report is presented of some coal carbonisation tests by the Heliopore process, which uses the waste heat in the exhaust gas of internal-combustion engines to carbonise non-coking coal or lignite. The gaseous products are distilled, and form part of the fuel supplied to the engine which drives an electric generator. The maximum value that can be assigned to the heat available in the engine exhaust gas does not exceed 6 or 7 cents per hr., and the economy thus effected does not justify much capital expenditure on plant; furthermore, the low temperature of the gas-engine exhaust militates against its efficient use, especially for carbonising coal.

**Gas at the New Kaiser Company Steel Plant at Fontana, California.** F. A. Herr. (American Gas Journal, 1943, vol. 159, Sept., pp. 11-13, 38). Particulars are given of the gas cleaning, distribution and utilisation at the iron and steel works which have just been erected at Fontana, California. The blast-furnace gas passes through a dust-catcher, a washer and two Cottrell precipitators to a large holder. The coke-ovens can be fired with either blast-furnace gas, or coke-oven gas, or a mixture of these. The coke-oven gas passes

through water-spray coolers, through a Cottrell precipitator to the saturator for removing the ammonia, and finally to a cooler and oil scrubber.

**Superimposed Precipitators for the Cleaning of Blast-Furnace Gas.** B. B. Frost. (*Iron and Steel Engineer*, 1943, vol. 20, Oct., pp. 54-61). A description is given of a blast-furnace gas-cleaning plant now being erected in the Chicago district in which three electric precipitator washer units are superimposed on the primary gas-washers; this system reduces the ground-space required and simplifies the lay-out of gas-mains and drains. The primary washers are 18 ft. in dia. and 52 ft. high, and each contains one rotor element immediately above the gas inlet, followed by three 3-ft. banks of drip-tiles. The spray header consists of twenty-six  $2\frac{1}{2}$ -in. nozzles capable of delivering 2340 gal. per min. at 10 lb. per sq. in. The washed gas contains a maximum of 0.25 grains of dust per cu. ft. Each precipitator unit is provided with 168 tubes 12 in. in dia., 15 ft. long. In periods of normal operation with blowing rates of 70,000-75,000 cu. ft. per min. on each of the two furnaces and the inlet gas at the precipitator containing 0.15 grains per cu. ft., the precipitator efficiency will be 96% with 0.006 grains per cu. ft. in the outlet gas with all three units working. When only two units are used the efficiency will be 88% and the dust content of the cleaned gas will be 0.018 grains per cu. ft. A negatively charged electrode hangs down the centre of each 12-in. precipitator tube, and the voltage across the 6-in. air-grap is usually maintained at about 75,000 V. A continuous flow of about  $1\frac{1}{2}$  gal. of water per min. carries the dust down the inside wall of each tube. Drawings of the plant are presented.

**The Economic Value of Colloidal Oil for Metallurgical Furnaces.** J. G. Coutant. (*Blast Furnace and Steel Plant*, 1943, vol. 31, Nov., pp. 1255-1257). Data on the advantages of using a suspension of coal in colloid form in fuel oil for heating forge furnaces are presented and discussed. The coal fines, which have passed through a 50-mesh screen, are mixed with oil in the proportion of 40% of coal to 60% of oil, and passed through a mill which reduces the coal particles to below 500 mesh. The statistics show that the cost of producing the "colloidal oil," as it is called, is small in relation to the increased heating efficiency obtained.

## PRODUCTION OF IRON

(Continued from pp. 120 A-121 A)

**A Study of Blast-Furnace Moisture Control.** J. J. Alexander. (*Blast Furnace and Coke Oven Association of the Chicago District and Eastern States Blast-Furnace and Coke Oven Association : Steel*, 1943, vol. 113, Nov. 29, pp. 89-94). An account is given of a

series of tests at a blast-furnace at Cleveland, Ohio, in which the changes in the silicon content of the iron and in the quantity produced with controlled and uncontrolled moisture in the blast were recorded. Wet- and dry-bulb temperature readings were taken for one month to ascertain the variations in the natural atmosphere. Subsequent test periods were run in which steam was injected into the blast, the quantity being adjusted to meet changes in the natural atmosphere, so as to maintain the total moisture constant at 4, 6, 8 and 11 grains per cu. ft. The most pronounced effect of controlling the moisture was to reduce the variations in the silicon content of the iron. The desired range of silicon was 0·65–0·95%, and, by keeping the moisture at 8 grains per cu. ft., the percentage of casts with the desired silicon was increased from 38·4% to 68·2%, the number of casts too high in silicon being thus appreciably reduced. The ratio of the weight of iron produced to that of all the solid materials charged was 1–2% higher with controlled moisture in the blast. The adoption of this control appears to have economic advantages, and further tests are being made.

**Thermal Reactions in Ferro-Alloy Metallurgy, the Basis of Alloy Steel Development.** B. D. Saklatwalla. (Joseph W. Richards Memorial Lecture : Electrochemical Society, 84th Convention, Oct., 1943). The theory and practical application of the reactions taking place in the preparation of the ferro-alloys used in the manufacture of alloy steels are reviewed under the following headings : (1) Inherent differences in the thermal balances in reductions with carbon, aluminium and silicon ; (2) fundamental basis of reducibility ; (3) graphic representation of reducibility by plotting the heats of oxide formation of the elements against their valencies ; (4) evaluation of deoxidisers ; (5) variation of heat of formation with conditions ; (6) commercial processes, with special reference to the alumino-thermic process of reduction ; (7) early furnace development ; and (8) the history of alloy steel development.

**Production of Sponge Iron.** É. Améen. (Iron and Coal Trades Review, 1944, vol. 148, Feb. 11, pp. 211–213 ; Feb. 18, pp. 249–251). An abridged English translation is presented of a paper describing the development at Söderfors of a suitable electric furnace and plant to operate the Wiberg process of making sponge iron. The article appeared originally in Jernkontorets Annaler, 1943, vol. 127, No. 8, pp. 277–315 (see p. 7 A).

**Presidential Address.** J. Tennent. (Journal of the West of Scotland Iron and Steel Institute, 1943–44, vol. 51, Part I., pp. 3–9). The address by the newly elected President of the West of Scotland Iron and Steel Institute is presented. It consists of a brief history of the development of iron manufacture in Coatbridge. It may be said that the iron era commenced in Coatbridge about 1830, when the introduction of hot blast by J. B. Neilson enabled the local Blackband ironstone to be successfully smelted with raw coal. Among many industrial pioneers, Baird of Gartsherrie and

Stewart of tube-making fame are perhaps the best known, and a brief account of their activities is given.

## FOUNDRY PRACTICE

(Continued from pp. 121 A-124 A)

**A Technical Department for Large Foundries Producing Small and Medium Castings.** H. Hayden. (Institute of British Foundrymen : Foundry Trade Journal, 1944, vol. 72, Jan. 20, pp. 47-51). A scheme to ensure complete co-operation between the designer, pattern-maker, foundry, finishing departments and machinists to ensure the more efficient production of large numbers of small and medium castings is outlined, and several examples of improvements in casting design and moulding practice which have resulted from it are described and illustrated.

**Ladle Inoculation Improves Gray Iron Properties and Structure.** H. W. Lownie, jun. (Foundry, 1943, vol. 71, Nov., pp. 126-128, 198-202 ; Dec., pp. 116-117, 194-197). The literature on the effects of silicon-bearing inoculants on the properties of cast iron is reviewed and some tests are reported the purpose of which was to ascertain whether the reactions between the inoculant and dissolved gases were responsible for the improvement in the properties of the iron. Two inoculants were used : (a) An alloy containing silicon 7%, manganese 7% and zirconium 7% ; and (b) commercial 94% ferro-silicon. The quantities of inoculant added are not stated directly, but for convenience the symbol  $\text{Si}^x$  followed by a percentage is used to denote a ladle addition sufficient to increase the silicon content of the metal by that percentage. Fairly large amounts of inoculant (a) were added to an iron containing 3.29% of total carbon and 2.05% of silicon ; the transverse strength showed a slight increase at first, but at above  $\text{Si}^x$  0.3% the value decreased. The transverse deflection increased rapidly up to  $\text{Si}^x$  0.4% and then decreased. Tensile strength and hardness were reduced with increasing silicon. Porosity and gas holes became apparent with  $\text{Si}^x$  above 0.95%. The sensitivity of the iron to changes in section thickness was at a minimum with  $\text{Si}^x$  at about 0.50%. The two inoculants (a) and (b) were similar in their effects. The results indicated that irons containing 3.02-3.27% of carbon and 1.00-1.65% of silicon benefit most by ladle inoculation.

**Foundry Pig Irons and Refined Irons.** E. Morgan. (Institute of British Foundrymen : Iron and Steel, 1944, vol. 17, Jan., pp. 220-223). **High-Duty Iron Castings.** E. Morgan. (Foundry Trade Journal, 1944, vol. 72, Jan. 27, pp. 67-72). The making of high-duty iron castings with special reference to the effect of phosphorus is discussed. Now that the import of low-phosphorus ores into Great Britain is very much curtailed, foundries have had to develop processes for

producing high-quality castings from charges comparatively high in phosphorus. This can be done by exercising proper control over the carbon and silicon contents. In the case of irons containing 1·5% of silicon, porosity due to shrinkage is likely to occur if the phosphorus exceeds 0·4% when the carbon exceeds 3·5%; with carbon below 3·4%, for the same silicon content, the phosphorus can be raised to 1·2%. When the casting section decreases, making it necessary to increase the silicon, a reduction in both carbon and phosphorus is necessary. Mixtures of phosphoric iron and low-phosphorus refined iron are now being successfully used without having to make ferro-alloy additions. When more than 15% of steel is incorporated in the cupola charge a special technique has to be employed to cope with the problems that follow. An incandescent bed of coke at least 36 in. above the tuyeres is necessary for high steel mixtures, and enough coke must be charged to maintain this bed at the proper height.

**Some Aspects of Sand Control.** F. Thomas. (Institute of British Foundrymen, 1944, vol. 72, Feb. 10, pp. 113-118). Experience in the operation and benefits of sand control at an iron and steel foundry is discussed. A synthetic green sand is used for almost the whole of the production; the advantage of this is that a higher degree of control of variables is possible than with naturally-bonded sands; unwanted oxides, such as ferrous oxide and lime, can be excluded, and last but not least, synthetic sand mixtures can be revived by adding bonding material. At this foundry 85% of all batch mixes consists of reclaimed sand. Coal dust for mixing with facing sand should contain about 32-35% of volatile matter, and 5-7% of ash is not detrimental.

**Notes on Oil-Sand Practice in the Ordinary Foundry.** W. Y. Buchanan. (Institute of British Foundrymen: Foundry Trade Journal, 1943, vol. 71, Dec. 9, pp. 291-293; 1944, vol. 72, Jan. 6, pp. 9-12; Jan. 13, pp. 35-37; Jan. 20, pp. 53-54; Jan. 27, pp. 75-76; Feb. 3, pp. 93-95). The following points relating to oil-sand practice are considered: Types of sand, especially those used in Scottish foundries; sand grain size; preparation of binders, storing and drying sand; plant for sand preparation, including the design and testing of mixers; drying and handling cores; design of core stoves; stack-moulding for repetition jobs; and the reclamation of oil-sand.

**Hydraulic Drive Spins Steel Casting Machines.** E. Bremer. (Foundry, 1943, vol. 71, Nov., pp. 154-157). Some particulars are given of the drive mechanism for centrifugal steel casting machines at the foundry of the Youngstown Alloy Casting Corporation. A hydraulic pump and drive have been devised which give a very wide speed range. Four 3-h.p. motors each drive two pumps in tandem, and the machinery is housed in pits with a vertical shaft protruding above floor level on which the flask is bolted. The steel is poured with the moulds spinning at about 100 r.p.m.

**Improved Casting Techniques.** J. L. Campbell. (*Steel*, 1943, vol. 113, Dec. 27, pp. 68-69, 101). Some particulars are given of the improved equipment and casting technique adopted by the Ohio Steel Foundry Co. to make cast steel breech-rings for 75-mm. guns. The steel is produced in a 20-ton and a 6-ton electric arc furnace. The moulds are prepared in large flasks accommodating up to eight patterns. The castings are allowed to cool in the mould for 6-12 hr., according to their size. The feeder heads are cut off and the castings ground, chipped, normalised, shot-blasted and sent to the machine shops.

## PRODUCTION OF STEEL

(Continued from pp. 124 A-125 A)

**The Economic Utilization of Alloy Steel Scrap.** H. Bull. (*Sheffield Society of Engineers and Metallurgists : Blast Furnace and Steel Plant*, 1943, vol. 31, Nov., pp. 1274-1279). Methods of dealing with alloy-steel scrap are discussed. The objectionable features of turnings are : low density, grease and oil probably containing sulphur, and variation in composition. The density of scrap can be expressed by a grade number which is the weight in hundred-weights of 1 cu. yard. The extent to which the grade number of turnings can be raised by passing them through a chipping machine varies with their composition and condition. Nickel-chromium steel turnings of 2-6 grade have been raised to grade 30 by chipping, whereas nickel case-hardening steel turnings were raised only to grade 18 by chipping in the same machine. Two procedures for working 18-ton heats with over 6 tons of turnings in the charge to produce chromium-nickel-molybdenum steel in a basic-lined electric furnace are described ; one is for single-slag working and the other for double-slag working. Stainless and heat-resisting steel scrap, unsuitable for remelting to reproduce similar steel, can often be used for raising the chromium in the charge, or for adding small amounts of chromium and nickel as final adjustments. The S.P.B. (*Sheffield Process Basic*) steel-making practice is described. This is a basic open-hearth process using charges so low in sulphur and phosphorus that they could be used in acid furnaces ; the pig iron charged is hematite iron. The charge put in the furnace contains all the elements required to give, when melted, the analysis called for in the specification, plus the usual margin of carbon. Proper conditions in the bath when melted are ensured by the charge containing about 0.5% of silicon and a maximum amount of manganese. Nickel-chromium-molybdenum steels can be made by this process, and high yields of the valuable alloying elements are obtainable from scrap charges. Melting and slag difficulties are

not experienced if the chromium-bearing materials are charged first and covered with carbon steel turnings, the limestone and iron being added last of all. The melted charge has a thin slag; the bath is allowed to get hot before ore is fed in small doses, the quantity depending on the carbon in the melt. The carbon falls quickly, and as equilibrium is approached the iron content of the slag falls and the boil is finally checked with ferro-silicon. In a typical 40-ton heat 6% of the chromium and about 70% of the manganese were lost during melting. Acid open-hearth furnaces appear to be least adaptable for alloy-scrap charges, but they can be used, and particulars of a heat are given.

**Current Metallurgical Problems in the Production of Cast Iron and Steel.** E. Zingg. (*Schweizer Archiv*, 1943, vol. 9, Aug., pp. 229-247). The difficulties encountered at the Sulzer Works, Winterthur, Switzerland, in the production of iron and steel under war-time conditions are discussed. The variety of scrap charged has greatly increased, and a statistical analysis was made of the chromium, nickel and copper contents of 777 heats of steel; frequency curves for these three elements were set up and a correlation was established between the nickel and chromium contents. Examples of the formation of cavities in 7-in. dia. cast-iron spheres are given. Cast iron showed a marked tendency to cavity formation when it contained unwanted elements which formed ternary or quaternary low-melting-point eutectics. Data on the impurities in the Jura-Dogger ores of Switzerland are presented, and the working of a 7-ton scrap charge with manganese additions in the form of briquettes made of Swiss manganese ore and coke breeze is described.

**Evaluation of Electric Arc Melting Furnaces.** W. H. Payne. (*Steel*, 1943, vol. 113, Dec. 6, pp. 124-126; Dec. 13, pp. 139-140, 148-150). Design details of electric-arc steel furnaces are described. In particular, American and European types of mechanism for controlling electrode movement are compared. In an American design of hydraulic electrode control, the electrode arm and moving parts and their counterweights are kept as light as possible to reduce the inertia; thus, small reversing metering pump motors can be used to move the fluid for the hydraulic movement of the electrodes. Originally the hydraulic unit was placed on the back end of the electrode arm supports; it is now placed on an accessible frame in the opening of the transformer room wall immediately adjacent to the furnace. Standard oil filters, valves and fittings are used throughout.

**Power Consumption of Electric Arc Furnaces.** F. Ryder. (*Blast-Furnace and Steel Plant*, 1943, vol. 31, Nov., pp. 1270-1273). The literature on some of the factors affecting the power consumption of electric arc furnaces is reviewed.

## REHEATING FURNACES

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(Continued from p. 82 A)

**A Modern Ingot Heating Furnace.** E. G. Smith. (Iron and Steel Engineer, 1943, vol. 20, Oct., pp. 62-65). The design of a modern reheating furnace for ingots is described. The furnace is square, with a single burner in the centre of the floor; the ingots are arranged round the burner, and the space in the centre forms the combustion chamber, so that the flame does not impinge on either the ingots or the refractory walls. The air is preheated in refractory recuperators of new design in which the waste gases pass downwards through straight thin-walled refractory tubes. The air is supplied by a low-pressure blower, and passes horizontally across the outside of the tubes and then upwards to a collecting flue leading to the burner. The cover normally rests in a deep sand seal, and the cover carriage lifts it vertically from the seal and traverses it to either side of the pit. The temperature is controlled at about 2400° F. by a thermocouple or radiation unit placed in the end wall of the pit at a level just above the top of the ingots.

**A New Soaking Pit Design.** J. Sparks. (Iron and Steel Engineer, 1943, vol. 20, Nov., pp. 48-52). A description is given of a new design of soaking pit, approximately rectangular in shape, in which the burners are placed opposite each other low down in the centre of the end walls and the ingots are placed in two lines near the side walls. The air is preheated to about 1000° F. by being blown through a silicon-carbide recuperator. Temperature control is obtained by thermocouples in recesses in the side walls near the top of the ingots.

## FORGING, STAMPING, AND DRAWING

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(Continued from pp. 125 A-128 A)

**Conservations through the Use of Stampings in Ordnance.** K. Rose. (Metals and Alloys, 1943, vol. 18, Oct., pp. 778-783). Some examples are given of the substitution of steel pressings for machined castings and forgings in ordnance parts which have resulted in the saving of material, machining time and cost.

**Upset Forging on a Flash Welding Machine.** (Steel, 1943, vol. 113, Nov. 29, pp. 74-75). Some examples are given of the application of flash-welding machines for the upset forging of round bars and tubing. Strongly built machines capable of exerting mechanical pressures of 8000 lb. per sq. in. have proved very suitable for the economic production of large numbers of upset forgings in medium carbon steel.

**The Relation of Fillets and Radii to Forging Die Design.** J. R. Thain. (*Heat Treating and Forging*, 1943, vol. 29, Nov., pp. 569-571). The importance of the fillet radius in relation to the life of forging dies is stressed, and a table is presented showing the increases in weight per inch length of fillet when the radius is increased in small stages from  $\frac{1}{32}$  in. to 1 in.; this increase is exceedingly small, and is always justified by the longer life obtained by making the radius as large as circumstances permit.

**The Formation of Sheet Metal Components by means of the Air-Operated Drop Stamp.** A. T. Pierce. (*Midland Metallurgical Society: Sheet Metal Industries*, 1943, vol. 18, Dec., pp. 2145-2148; 1944, vol. 19, Jan., pp. 109-116). The development of the air-controlled drop stamp and its advantages are described. Its two main advantages in comparison with ordinary rope drop hammers are: (1) All operations can be easily controlled; and (2) the sensitivity of the mechanism enables the operator, without fatigue, to move the ram rapidly and with as much pressure as the work requires, at the same time keeping the work under visual supervision. A brief outline of the order of operations from the tool design to the finished pressings, in particular for aircraft parts, is given.

**Continuous Production Line for Tubular Railway Axles.** (*Iron and Steel Engineer*, 1943, vol. 20, Nov., pp. 78-79). A description is given of the plant and process used by the Pittsburgh Steel Co. to make hollow axles for rolling stock. This process has already been described in an article entitled "Tubular Railway Axles" (see p. 126 A).

**Forming Heavy Plate on a 6000-Ton Press.** G. E. Stedman. (*Metals and Alloys*, 1943, vol. 18, Nov., pp. 1064-1069). A brief illustrated description is given of the plate-bending press at the Chattanooga plant of the Combustion Engineering Co., Incorporated. It is capable of cold-bending boiler plate up to 6 in. thick in lengths of up to 40 ft. The press consists of two 3000-ton, 4-post hydraulic presses connected by two built-up beams. The upper movable beam is 52 ft. long and 14 ft. deep at the centre. The two main rams are 52 in. in dia. and operate at 1500 lb. per sq. in., which can be intensified to 3000 lb. per sq. in. For the thick shell plates of pressure vessels the carbon and manganese contents of the steel are limited to 0.35% and 0.90%, respectively.

**The Presspun Process of Dishing and Flanging.** (*Engineering*, 1944, vol. 157, Feb. 11, p. 116). A brief description is given of a spinning and flanging press with which very heavy work can be undertaken; the example given is a dome-shaped head of mild steel 9 ft. 1 in. in dia.,  $5\frac{1}{4}$ -in. thick, formed to a spherical radius of 6 ft. 8 in. and a knuckle radius of 11 in., weighing 10 tons 13 cwt. The machine consists in the main of two heavy vertical columns of welded steel joined together at the top by deep horizontal girders. The girders carry a vertical hydraulic cylinder, the ram of which

terminates in a circular platen opposed to a similar platen, or table, at the base of the machine. The platens are shaped to suit the contour of the head to be formed, and the heated plate is gripped tightly between them. The whole assembly of platens and work is then rotated round its vertical axis. At one side of the base, and near the edge of the bottom platen, is a vertical roller, the distance of which from the axis of the assembly is adjustable. In line with this is a second roller carried in a saddle mounted so that the roller can be moved from a position in which its axis is horizontal to one in which it is vertical. The saddle is traversed in a radial direction relative to the platen assembly by a motor drive through a worm reduction gear. Apart from the fact that its use eliminates the frequent reheatings necessary in the usual flanging methods, the "Presspun" process gives a much wider range of choice in design, since a series of expensive die-blocks is not required.

**"Spinnability" of Metals is Reduced to a Numerical Factor Indicating Performance to be Expected.** (Steel, 1943, vol. 113, Nov. 29, p. 84). An American firm which has had a long experience in the spinning of metals and alloys publishes a table of the relative "spinnability" of a variety of materials including several qualities of steel; of the latter, cold-rolled deep-drawing quality is given the highest rating.

**Automatic Forging of 90-mm. Shells.** (Machinery, 1944, vol. 64, Jan. 27, pp. 95-96). The automatic forging of 90-mm. shells from square steel billets in four stages in a single machine at the works of the General American Transportation Corporation is described.

**The Manufacture of Steel Cartridge Cases.** H. R. Turner. (Metals and Alloys, 1943, vol. 18, Oct., pp. 771-777). The general aspects of the problem of making steel cartridge cases are considered, and the processes employed by the Auto-Lite Co. of Cincinnati in the manufacture of 20-mm. cases are described and illustrated. The quality of the raw material is of vital importance, and an aluminium-killed and spheroidised steel cast in big-end-up hot-top moulds is used, the analysis being carbon 0.22-0.32%, manganese 0.45-0.75%, silicon 0.10% max., phosphorus 0.040% max. and sulphur 0.045% max. A flat disc is first drawn into a cup; this is annealed, drawn, cleaned, annealed again, coated with a soap solution, drawn a third time, alkali-cleaned, trimmed, drawn twice more, headed, tapered, finally trimmed, alkali-washed, stress-relieved, pickled, washed, dried and inspected.

**The Principles of Lubrication in Modern Deep-Drawing Practice.** H. A. H. Crowther, P. D. Liddiard and K. I. Marwood. (Sheet Metal Industries, 1943, vol. 18, Oct., pp. 1733-1738; Nov., pp. 1915-1920; Dec., pp. 2099-2105; 1944, vol. 19, Jan., pp. 81-83, 88). In the first part of this paper the theory of lubrication is explained, and it is shown that in deep-drawing there are three main criteria which serve to make the lubrication conditions different from those applicable to fluid lubrication; these are the total

operating pressure, the distribution of that pressure and the rise in temperature which occurs. From a consideration of these it is seen that the basic requirements for successful deep-drawing lubrication are : (1) The area of actual contact between the metals must remain small ; (2) the metals should be prevented as far as possible from coming within the zone of attraction of each other ; and (3) the temperature must be kept to the minimum by, for example, the presence of sufficient of a low-melting-point metal. In the second part, after a brief discussion of the properties of deep-drawing tools, the relative merits of mineral oils, fatty oils, waxes, metallic soaps, soluble oils, chlorinated hydrocarbons, lubricants with addition agents such as sulphur, phosphorus and nitrates, and finally, solid lubricants are dealt with in the light of the theories put forward in the first part. In the third part the chemical, mechanical and health factors influencing the choice of lubricant are considered. The concluding part includes descriptions of methods of applying and removing the lubricant in different types of drawing operations.

**The Technique and Advantages of Employing Tungsten Carbide Inserted Dies.** E. J. Swinn. (*Sheet Metal Industries*, 1944, vol. 19, Feb., pp. 297-300). Recommendations on the design and use of tungsten-carbide dies are made. When drawing solid bar and wire, a drawing angle of 10-12° usually gives good results for hard steel, whilst 14-16° is more usual for softer steel. Although wide drawing angles reduce the drawing load, they cause a more abrupt deformation of the material and greater work-hardening. The die nib or insert must be firmly supported in a case of ample dimensions, so that it is impossible for it to expand. The hardest grades of insert may be employed where the stress is light, but the tougher grades are essential for grades which are highly stressed. It is of vital importance that relapping is carried out as soon as inspection indicates that a wear ring is being formed in the drawing angle.

**The Development of Sintered Tungsten Carbide Drawing Dies.** E. J. Sandford. (*Sheet Metal Industries*, 1944, vol. 19, Jan., pp. 129-134). A comprehensive account of the manufacture of sintered tungsten-carbide drawing dies with data on their properties is given. The sequence of processes following the preparation of the tungsten-carbide and cobalt powders is : Mixing in a ball-mill with a stainless-steel shell plate and tungsten-carbide balls, pre-sintering at 750-1000° C. for about 30 min., machining the pre-sintered die to size, and final sintering in hydrogen at 1400-1500° C.

**The Drawing of Fine Uncoated Steel Wire.** R. R. Preston. (*Wire and Wire Products*, 1943, vol. 18, Dec., pp. 763-767). The drawing down of uncoated steel wire from an initial diameter of 0.036 in. is described. After patenting, the wire must be cleaned in either cold hydrochloric acid or sulphuric acid at 120-130° F. The wire is then rinsed and limed. Air-slaked lime is undesirable for any kind of wire-drawing requiring more than two drafts. After slaking, the lime should be "aged" in a putty-like condition

for 30–60 days. The lime solution is held at about 180° F. in the dipping operation and the wire is dipped in 4–6 times. Baking at 300–350° F. is the next operation. The first draft is a "skin draw," with soap as a lubricant, in which the diameter is not reduced by more than 0.002 in. In succeeding drafts a reduction of about 25% per draft is satisfactory. The die for the first pass has an opening angle of 30° blending into an approach angle of 12°; the bearing length is at least 75% of the wire diameter. Every plant has its own correct speed for drawing fine uncoated steel wire of different carbon contents. Modern continuous machines can draw at speeds of from 800 to 2200 ft. per min.

## ROLLING-MILL PRACTICE

(Continued from pp. 82 A–83 A)

**The Calculation of Roll Pressure in Hot and Cold Flat Rolling,**  
 E. Orowan. (Proceedings of the Institute of Mechanical Engineers, 1943, vol. 150, No. 4, pp. 140–167). A numerical or graphical method is given for computing, in strip or plate rolling, the distribution of roll pressure over the arc of contact and the quantities derived from this (*e.g.*, the vertical roll force, the torque and the power consumption). The method avoids all mathematical approximations previously used in the theoretical treatment of rolling, and permits any given variation of the yield stress and of the coefficient of friction along the arc of contact to be taken into account. It can be used therefore in both hot- and cold-rolling, provided that the basic physical quantities (yield stress and coefficient of friction) are known. It is found that the discrepancy between the roll pressure distribution curves calculated from the Kármán theory and those measured by Siebel and Lueg is due to the assumption in the theory that the frictional drag between the rolls and the rolled stock is equal to the product of the roll pressure and the coefficient of friction. If frictional effects are dominant, as in hot-rolling, this product may easily exceed the yield stress in shear which is the natural upper limit to the frictional drag, and then static friction instead of slipping occurs. This has been taken into account in the present method, and the calculated curves of roll-pressure distribution show good agreement with the curves measured by Siebel and Lueg.

**Substitute Materials in Steelworks Machinery (in Germany).**  
 E. Rohde. (Iron and Steel Institute, 1943, Translation Series, No. 160). An English translation is presented of a paper which appeared in Stahl und Eisen, 1943, vol. 63, Feb. 4, pp. 85–94. Suggestions are made by which the consumption of copper in mill bearings and in collector shoes for electric overhead cranes is reduced (*see* Journ. I. and S.I., 1943, No. I., p. 161 A).

**Scheduling the Primary Mills.** A. Montgomery, jun., and J. B. Holbrook. (*Iron and Steel Engineer*, 1943, vol. 20, Nov., pp. 62-67). A description is given of the system employed by the Carnegie-Illinois Steel Corporation for planning the production of steel and its allocation to the soaking pits, roughing mills and blooming mills. The system involves the use of planning boards which indicate the expected tapping times of the open-hearth furnaces and boards for each mill-stand which are used in making up the rolling programmes.

**The Design of Blooming and Slabbing Mill Elements.** H. H. Talbot. (*Iron and Steel Engineer*, 1943, vol. 20, Nov., pp. 37-47). Some details in the design of two-high, motor-driven, reversing, blooming and slabbing mill-stands and auxiliary equipment are considered and calculations of the roll pressures and other forces are presented.

**Roll More Tons. VI.** A. E. Lendl. (*Iron and Steel*, 1943, vol. 17, Dec., pp. 173-179). Continuation of a series of articles (see p. 16 A). In this part the calculation method shown in the previous articles is applied to the first pass of beam calibrations and to the first forming passes of angles, T-bars and channels.

**New 140-Inch Plate Mill at Alabama Plant.** J. D. Clark. (*Iron and Steel Engineer*, 1943, vol. 20, Oct., pp. 35-42). An illustrated account is given of how a plate mill of the Tennessee Coal, Iron and Railroad Company was enlarged. The original three-high 110-in. stand is now used as a roughing mill and a new 140-in. four-high stand serves for finishing. The mill can now produce plates up to 128 in. wide, 60 ft. long and  $\frac{3}{16}$ - $1\frac{1}{4}$  in. thick.

**Main Roll Drives for Blooming and Slabbing Mills.** R. H. Wright. (*Iron and Steel Engineer*, 1943, vol. 20, Nov., pp. 55-59). The development of electrically driven blooming and slabbing mills in the United States is reviewed. Curves showing the relation between torque, speed and horse-power in reversing motor requirements are presented and examples of calculations of the power requirements for certain rolling operations are given.

**The Problem of the Cold Mill Drive.** R. P. E. Tabb and A. M. Fletcher. (*English Electric Journal*, 1943, vol. 10, No. 8, pp. 174-179). Methods of driving and controlling single-stand cold strip mills and problems connected therewith are discussed, with special reference to the advantages of the Ward-Leonard system in which the mill motor is fed from a D.C. generator driven at constant speed.

**Three-Roll Straightening Machine.** (*Sheet Metal Industries*, 1944, vol. 19, Feb., pp. 251-252). A brief illustrated description is given of the Medart roller straightening machine for tubes and bars. In this machine a pair of duplicate rolls are placed opposite a single concave roll which makes contact with the tube or bar between the two points of support afforded by the other two rolls. Straightening is accomplished without pressure being exerted directly across the

diameter; this is particularly important when butt-welded tubes are being straightened.

**Flying Shear Electric Tie.** J. D. Campbell. (Steel, 1943, vol. 113, Nov. 22, pp. 85-88). In order to cut off pieces of equal length from strip issuing from a continuous hot strip mill it is necessary to have a means of synchronising the flying shears with the last stand of the mill. A hydraulic and an electric method of effecting this synchronisation or "tie" are described. The electric tie employs amplidyne control to coarse and fine speed-matching units; one installation has given nearly three years satisfactory service.

## PYROMETRY

(Continued from pp. 83 A-84 A)

**Automatic Pyrometer Control of High-Speed Salt Baths.** (Steel, 1943, vol. 113, Nov. 22, pp. 78-80). A brief description is given of a temperature measuring and control unit designed for use with electric salt-bath hardening furnaces for high-speed steel tools in which the rate of heating is very rapid. A wrought-iron tube has a socket at one end, into which a sillimanite target tube 12 in. long is inserted, and a radiation-measuring cell called a "RADIAMATIC," fixed in the upper end; this cell is connected to a potentiometer recorder which operates an "on and off" controller in the furnace element circuit. When in use the sillimanite tube is dipped 4 or 5 in. below the surface of the bath. This sillimanite pyrometer is intended for barium-chloride salts and is unsuitable for cyanide baths.

**Barrier-Layer Photo-Electric Cells for Temperature Measurement.** T. Land. (Iron and Steel Institute, 1944, this Journal, Section I.). The selenium barrier-layer photo-electric cell offers many advantages for the measurement of temperatures in the foundry. Such cells have previously been used for temperature measurement, but little has been known about their limitations or their calibration. Ten cells were investigated and their fatigue, their temperature coefficients and their departure from linear response were determined. The calibration of each cell was established, using a black-body furnace and a tungsten-ribbon-filament lamp as sources of radiation. The theoretical investigation shows the relation of the calibration to the spectral sensitivity and the correction which must be applied when a tungsten lamp is used as a temperature standard. It was established that if allowance was made for the small differences in sensitivity between individual cells (about  $\pm 4\%$ ), a single table adequately represented the calibration of the cells. Nine of the ten cells proved satisfactory for temperature measurement. The design of the optical system and its effect on the calibration of the pyrometer were studied

theoretically and experimentally, and a basis for the design and calibration of pyrometers was laid down.

**The Drift of Selenium Photo-Electric Cells in Relation to their Use in Temperature Measurement.** J. A. Hall. (Iron and Steel Institute, 1944, this Journal, Section I.). The paper describes experiments made to investigate the "drift" effect in selenium barrier-layer photo-electric cells intended to be used for temperature measurement. It was found that the drift of seven of the nine cells examined was too great to permit of their use for the most accurate work. However, a comparison with work done by Land showed that his cells were, on the average, more satisfactory and that, by pooling the two batches, eleven satisfactory cells could be obtained from a total of nineteen.

The following characteristics of the drift effect were noted. The drift, expressed as a percentage, is independent of the current given by the cell, and hence of the brightness to which the cell is exposed. If a cell is allowed to drift by exposure to radiation from a source at a given temperature and the temperature is then increased, the initial response to the higher temperature is almost, but not quite, as great as if the cell had not previously drifted at the lower temperature. Drift is much reduced when deep-red and infra-red radiation is excluded. Among the filters examined, a  $\frac{1}{4}$ -in. thickness of Calorex glass was sufficient to obtain the maximum observed reduction in drift (about 50%). No drift was observed when the cell was exposed on open circuit. If the illumination of a cell is interrupted for a short period and then resumed, the sensitivity of the cell recovers somewhat during the "rest" period, but rapidly resumes the value it had had just before, irrespective of whether it had previously been allowed to drift for a long or a short period. The speed of recovery depended to some extent on the circuit conditions under which the cell was allowed to recover, and was most rapid when the cell was short-circuited.

**The Emissivity Characteristics of Hot Metals, with Special Reference to the Infra-Red.** D. J. Price and H. Lowery. (Iron and Steel Institute, 1944, this Journal, Section I.). The theoretical and practical considerations in connection with the study of emissivity are discussed and the relevant literature is critically surveyed. The application of emissivity data to the correction of pyrometer readings has been examined and the necessity of an adequate knowledge of emissivity data is indicated. The information at present available does not meet this need, especially in the important case of iron, and, in view of this, suggestions for future experimental researches are noted.

Correlation of all available data appears to indicate a zero temperature coefficient of emissivity (for all substances) at a specific wave-length in the infra-red region. This implies that at a certain wave-length peculiar to each substance the emissivity correction to a pyrometer would take a much simpler form than at present.

**A Thermocouple Method for the Measurement of Liquid Steel Casting-Stream Temperatures.** D. A. Oliver and T. Land. (Iron and Steel Institute, 1944, this Journal, Section I.). A new method of measuring the true temperature of the liquid steel in the casting stream is described. A platinum/platinum-rhodium thermocouple, lightly sheathed in silica, was allowed to protrude into the narrow part of the conical refractory lining of a runner box. The e.m.f. of the thermocouple was applied to a mains-driven high-speed amplifier and recorder, which showed that a steady temperature was attained in approximately 15 sec. The application of the method is illustrated by two investigations. The first was on the emissivity of a nickel-chromium-molybdenum steel, which was deduced from the comparison of optical pyrometer readings and the true temperatures measured by the thermocouple. In the second investigation thermocouple readings of the ladle stream temperature were compared with the recorded temperatures of the metal in the furnace before tapping, from which the ladle cooling of the liquid steel was deduced. The results showed gratifying consistency and the procedures proved simple and reliable.

## HEAT TREATMENT

(Continued from pp. 128 A-131 A)

**The Uses of Controlled Atmospheres in the Metal Industries.** (Sheet Metal Industries, 1943, vol. 18, Sept., pp. 1535-1540, 1544; Nov., pp. 1900-1905, 1912; Dec., pp. 2087-2093, 2096; 1944, vol. 19, Jan., pp. 61-66; Feb., pp. 243-250). In Part I. of this series of articles, the oxidising, reducing, carburising or decarburising effects of different gas mixtures on iron and steel are explained with reference to curves showing the equilibrium values of the water-vapour/hydrogen, carbon-dioxide/carbon-monoxide and methane/hydrogen ratios at different temperatures. It cannot be assumed that because a gas is reducing in character it will at the same time be decarburising, and the absence of free oxygen is not sufficient to ensure that an atmosphere will not be oxidising. The advantages of electric furnaces for heat treatment with controlled atmospheres are pointed out. In Part II., some of the better-known furnace atmospheres are discussed, in particular charcoal gas and those derived from burning coal gas, producer gas and coke-oven gas. An important advantage of charcoal gas is that it is a simple atmosphere consisting of carbon monoxide and nitrogen with very little carbon dioxide, hydrogen and water vapour; its composition is easily controlled by regulating the flow of air through the charcoal bed in the generator. In Part III., methods of producing partially burned cracked ammonia, as well as cracked propane and butane, are described and brief reference is made to the use of controlled

atmospheres for hardening, tempering, annealing, normalising, carburising and nitriding. The heat treatment of non-ferrous and of ferrous metals are dealt with in Parts IV. and V., respectively. A furnace atmosphere often consists of five gases, not counting impurities, and, as iron has three oxides, the number of possible reactions in the heat-treatment furnace is very large. The effects of carbon dioxide, carbon monoxide, oxygen, hydrogen, methane, water-vapour, nitrogen and of the water-gas reaction are considered. In an atmosphere containing appreciable quantities of carbon monoxide, any accidental leakage of water vapour into the furnace will be rendered less serious than expected because it will be partly converted into carbon dioxide and hydrogen, whereas gases consisting mainly of nitrogen have not the ability to compensate for moisture accidentally introduced into the furnace.

**Notes on the Heat Treatment of Grey Cast Iron.** M. Bader. (*Schweizer Archiv*, 1943, vol. 9, May, pp. 148-156). The following forms of heat treatment of grey cast iron are discussed : (1) Stress-relieving ; (2) full-annealing ; (3) hardening and tempering ; (4) hot-bath or two-stage hardening ; and (5) flame-hardening. Stress-relieving is achieved by annealing at a temperature in the 100-500° C. range selected so that the pearlite matrix is not appreciably affected and the temperature of graphite formation is not reached. In full-annealing, on the other hand, the object is to promote the breakdown of the pearlite ; the temperature and holding time must be related to the carbon and silicon contents. If the hardening temperature is above the pearlite interval (*i.e.*, the temperature range in which the ferrite, austenite and carbide are in equilibrium) a fully martensitic structure results, but if the iron is quenched from a temperature in the pearlite interval, the structure is mostly ferrite with the remainder martensite. The hard martensite can be transformed to softer troostite or sorbite by tempering at a suitable temperature. The results of a large number of heat-treatment tests on two cast irons are presented and discussed, particular attention being paid to the use of S-curves to determine the correct quenching temperature and holding time in the two-stage hardening of cast iron.

**"Heat" Treating at 120° below Zero.** G. W. Birdsall. (*Steel*, 1943, vol. 113, Dec. 27, pp. 70-74). The heat treatment of gauges and gauge blocks to stabilise them and prevent subsequent growth is discussed. A transformation diagram for high-speed steel shows that the proportions of austenite retained after quenching to 400° F. in oil and subsequent cooling are : 60% at 300°, 15% at 100°, 10% at 70° and 3% at -120° F., the 10% left at room temperature, if no further cooling is applied, transforms very gradually and accounts for the growth. At some works gauges are stabilised by holding at -120° F. for 2 hr., followed by 2 hr. in boiling water and 2 hr. more at -120° F. The heat-treatment cycles with refrigeration adopted by a number of American works are given.

**Application of Salt Baths in the Heat Treatment of Forgings.** H. Solakian. (*Heat Treating and Forging*, 1943, vol. 29, Nov., pp. 585-587). The advantages of using electrically heated salt-bath furnaces for the heat treatment of forgings to prevent overheating, decarburising and scaling are discussed.

**Salt Bath Hardening of NE Steels.** L. J. Sheehan. (*Metals and Alloys*, 1943, vol. 18, Nov., pp. 1087-1091). Some experiences in the hardening of NE steels in electrically heated salt-baths are related. The silicon-manganese steels are very susceptible to decarburisation, but gears of this steel have been successfully hardened in a salt bath. The furnace used has a pot 40 in. deep; it is a standard 60-kW. Ajax-Hultgren unit with closely spaced electrodes immersed to within 12 in. of the bottom of the pot.

**Heating Gears for Hardening by High-Frequency Induction.** F. W. Curtis. (*American Gear Manufacturers' Association : Machinery*, 1944, vol. 64, Feb. 3, pp. 119-124). Factors affecting the induction-hardening of gears are considered. With this process a steel with a higher carbon content can usually be substituted for a carburising steel, and, as a steel with 0·40-0·50% of carbon is only slightly more expensive than the same type of steel with a low carbon content, induction-hardening without carburising can be applied with a saving in cost. With gears having small teeth of about 20-pitch, the entire tooth is heated; with larger teeth of about 12-pitch, the heat pattern across the section begins to follow the contour of the tooth. When the teeth are 8- or 10-pitch the heat follows the tooth contour almost exactly, and this gives the best and most uniform case-hardening. With larger teeth, such as 4-pitch, the heat pattern resembles that for fine teeth. The heating cycles for a number of different-sized gears using a 35-kW. converter operating at a frequency of about 300 kilocycles are given.

**New Automatic Induction Fixture Speeds Halftrac Sprocket Hardening.** (*Industrial Heating*, 1943, vol. 10, Nov., pp. 1662-1664). A brief description is given of the equipment used in conjunction with an induction-hardening machine for hardening the teeth of 12-in.-dia. sprockets for tank tracks. Two sprockets are mounted horizontally one above the other, and the automatic device pushes them forward so that two teeth at a time enter the heating coils, withdraws and turns them, and pushes forward the next two teeth. The hardening cycle consists of 10 sec. heating, 4 sec. quenching and 6 sec. for movement.

**The Scaling Properties of Steels in Furnace Atmospheres at 1150° C.** A. Preece and R. V. Riley. (*Iron and Steel Institute, 1944, this Journal, Section I.*). The rate of oxidation and the character of the oxide formed in furnace atmospheres at 1150° C. were examined for a selection of carbon and alloy steels. An account is given of the important influence of sulphur dioxide and free oxygen in the furnace atmosphere in governing the process of oxidation. It was found that each of the alloy steels behaved in a characteristic manner.

and generalisations are difficult. The formation of sulphide complexes at the scale-metal interface observed in earlier experiments at 1000° C. also occurred at 1150° C., and they behaved in a similar manner by inducing intercrysalline penetration of scale into the metal in all the steels except those containing appreciable quantities of silicon, chromium and aluminium. With these three latter types of steel preferential oxidation of the alloying element produced a protective oxide film, and continued oxidation was possible only under conditions of temperature and furnace atmosphere where the film became unstable. Factors which influence the instability of these films are discussed.

**Flakes and Their Prevention.** O. A. Bamberger. (*Iron and Steel Engineer*, 1943, vol. 20, Nov., pp. 68-73). An account is given of an investigation of different heat treatments with the object of finding one to prevent flake formation in ingots of a 1%-carbon 1.5%-chromium steel. Flake formation was prevented by cooling in air to below the  $Ar_1$  point, reheating and soaking at above the  $Ar_3$  point, and then cooling at any speed to obtain the hardness desired. A second series of tests proved that flaking did not take place until the temperature to which the steel was allowed to cool before reheating was 400° F. or less. The heat treatment eventually adopted in the forge shop in question was : Cooling in air to 1000° F., soaking at 1000° F. for 4 hr., reheating to 1500° F. in 5-6 hr., soaking at 1500° F. for 5 hr., and cooling in air or in the furnace as desired.

**The Pressure Quench for Armor Plate.** F. P. Peters. (*Metals and Alloys*, 1943, vol. 18, Oct., pp. 789-794). An illustrated description is given of the "Drever" pressure-quenching machine. The purpose of this machine is to prevent the distortion of light armour plate when it is quenched on leaving the hardening furnace. The plate passes over a horizontal roller conveyor until it is in position between two grid-like platens ; the lower platen is raised by hydraulic pressure until it holds the plate against the upper platen ; two banks of water sprays, one above and one below the plate, are then turned on so that both sides of the plate are simultaneously and uniformly quenched.

**Secondary Hardening of High-Speed Steel-Cutting Tools.** J. Garland. (*Machinery*, 1944, vol. 64, Jan. 27, pp. 91-94). The theory and practice of the hardening of high-speed steel are discussed. If, after primary hardening, the tools are ultimately cooled in an oil-bath at about 100° F. and held for at least 15 min. after attaining this temperature before tempering, risks from cooling stresses would be minimised. It should be made certain that sufficient time is allowed for the primary hardening transformation to take place at the minimum temperature reached during cooling from the high-temperature treatment before proceeding with the tempering. The first step in tempering is the softening of that proportion of primary martensite which forms during cooling from

the hardening temperature. The second step changes the remaining larger proportion of austenite into secondary martensite. In general, the temperature at which the first step takes place on cooling is raised with increase of the tempering temperature and with the holding time at that temperature. It takes place below about 245° C. after tempering 18/4/1 high-speed steel for 2½ hr. at 565° C. Maximum effectiveness of high-speed steel tools is secured when they are treated to yield maximum hot-hardness, but maximum cold-hardness does not necessarily indicate maximum hot-hardness. A procedure for determining whether tools have been properly tempered is as follows: (1) Test each tool for hardness, which should not be less than Rockwell C 64, or about Vickers D.P.N. 800; (2) heat one or more of each consignment to 340–360° C. and retest for hardness. A loss of hardness indicates that the tool being tested has not been tempered.

## CLEANING AND PICKLING OF METALS

(Continued from pp. 93 A–94 A)

**Factors Affecting the Strength of Soldered Joints Made from Electro-Tinned Steel Sheet.** A. W. Hothersall, D. W. Hopkins and G. L. Evans. (Iron and Steel Institute, 1944, this Journal, Section I.). The effect of the method of cleaning steel sheet in preparation for electro-tinning on the strength of soldered joints has been investigated, using a tearing test. The effect on the joint strength of the weight of tin coating, the time of storing the plated sheet before soldering and the type of solder were also examined. The method used for cleaning the steel sheet in preparation for electro-tinning had a marked effect upon the strength of the soldered joint as determined by a tearing test, especially when an acid tin bath was employed. With the acid bath the type of cleaning cycle ordinarily used in electroplating practice gave low joint strengths, and the initially low strength further decreased appreciably on heating the plated sheet before soldering to the temperature required for stoving tinplate lacquers. It was found that, by treatment in an alkaline solution after pickling and immediately before plating in the acid bath, joint strengths were markedly improved and no loss in strength was produced by stoving the plated sheets before soldering. Methods of applying this discovery to the electro-tinning of sheet were investigated, and suitable procedures are indicated. Using this pretreatment in alkaline solution, joint strengths for any given steel sheet and method of pickling were closely similar with the acid electrolyte to those obtained with the sodium stannate bath and were at least equal to those given by hot-dipped tinplate made from similar steel. Joints soldered after

storage of the electro-tinned sheet were less strong than when the sheet was freshly tinned. With dry storage the strength fell in sixteen weeks by 10% (sodium stannate bath, 4-oz. coatings) and 15% (acid tin bath, 4-oz. coatings, with pre-treatment in alkali). The deterioration in joint strength was more rapid when soldering followed storage in a corrosive atmosphere. Soldered joints increased in strength on keeping for sixteen weeks, the amount of the increase varying with solder containing 40% of tin from 6% to 30%, according to the conditions of electro-tinning. With solder containing 60% of tin the increase was greater (up to 70%).

**Snagging Castings.** G. S. Eisaman. (*Foundry*, 1943, vol. 71, Nov., pp. 119-120, 173-176). Swing-frame grinding machines and the grinding technique for trimming castings are described, and comprehensive information is given on the composition, bond, grain size and speed of the grinding wheels for use on different metals and alloys.

## COATING OF METALS

(Continued from pp. 95 A-100 A)

**A Sulfate-Chloride Solution for Iron Electroplating and Electro-forming.** R. M. Schaffert and B. W. Gonser. (*Electrochemical Society*, Oct., 1943, Preprint No. 84-25). The restrictions in the use of copper and nickel for making type have stimulated interest in the electrodeposition of iron. The results of tests with an iron-plating solution developed at the Battelle Memorial Institute are presented and discussed. The solution is made up of 250 g. per litre of ferrous sulphate, 42 g. per litre of ferrous chloride and 10 g. per litre of ammonium chloride. This bath remains stable over long periods and the iron deposits produced are less brittle than those made with the ordinary sulphate or chloride baths.

**Properties of Hard Chromium Plate.** J. J. Dale. (*Australian Institute of Metals : Australasian Engineer*, 1943, vol. 43, Oct. 7, pp. 25-31). The process of chromium plating is described and the properties of the coating discussed. In chromium plating, the chromium is present in the hexavalent form in the anion  $[\text{CrO}_4]$ . That it should be deposited at all under these conditions seems remarkable. Modern theory postulates the existence of a colloidal film of chromium chromate or dichromate, around the cathode, within which direct reduction to chromium from the hexavalent form to the metal is brought about by atomic hydrogen formed at the cathode. The presence of sulphate, or another anion, is necessary to condition this film so as to permit of the optimum diffusion of chromate ions through it. The density of cast chromium is reported as 7.1 g. per c.c., but that of electrolytic chromium is slightly

less, at between 6.92 and 6.95. The melting point of chromium is often quoted at values between 1520° and 1615° C., but recent determinations on metal of increasing purity indicate that the true melting point is probably 1900° C. at least. Widely divergent electrical resistivity values have been published; A. B. Kinzel and W. Crafts give it as  $13.1 \times 10^{-6}$  ohm-cm. The coefficient of expansion is given in the International Critical Tables as  $8.1 \times 10^{-6}$  in. per in. per °C. Electrolytic chromium, however, actually contracts on first heating, due to the expulsion of hydrogen; its coefficient of expansion is considerably lower than that of the metals on which it is likely to be deposited. By varying the plating conditions it is possible to produce deposits ranging in hardness from 400 to 1200 (diamond pyramid hardness scale). Information on other properties is quoted from the literature, with special reference to the work of M. Cymboliste (*see Journ. I. and S.I.*, 1938, No. I., p. 351 A).

**Continuous Plating of Fine Steel Wire with Nickel.** J. H. Conolly and R. Rimbach. (Electrochemical Society, Oct., 1943, Preprint No. 84-22). A description is given of the process of nickel-plating steel wire to be used instead of solid nickel wire for supporting the filaments in electric lamps. After various cleaning operations, the wire is passed through a concentrated Watts' nickel-plating solution at a speed of 12 ft. per min. The bath is held at 60° C. and a pH value of 2.0; the current density is between 200 and 600 amp. per sq. ft. A very adherent nickel deposit 0.005 mm. thick is obtained which will withstand sharp bends without cracking. These nickel-plated wire supports last as long as the filaments.

**Electro-Galvanising of Wire.** (Iron and Coal Trades Review, 1944, vol. 148, Jan. 21, pp. 92-94; Wire Industry, 1944, vol. 11, Jan., pp. 27-29). A description is given of the Bryanising system for the continuous electrodeposition of zinc on wire. After patenting, the wire is passed through a caustic-soda cleaning bath held at about 450° C. As each length of wire enters the bath it is charged with cathodic current; this liberates sodium from the bath, which combines with the oxygen in any adhering scale. After passing through rinsing baths, the wire moves along the galvanising tanks or plating cells. At one plant these cells are 94 ft. long in groups of four, side by side. Sixteen lengths of wire pass simultaneously on parallel courses through each cell, and on each wire rides a series of cathodes spaced at equal distances. The anodes in each cell are strips of insoluble silver-lead alloy, the zinc deposited on the wire being drawn entirely from the electrolyte. The construction of the cells is like an elongated water-trough of iron with a hollow lining of lead, through which water is circulated as a cooling medium. The success of the process is due largely to the fact that the electrolyte—an acid solution of zinc sulphate—can be prepared to a purity of 99.999%. The wire is made to rotate slowly as it passes through the cell, so that the deposition is uniform around the surface. The wire is drawn down to the required gauge after galvanising.

**The Electrogalvanizing of Strip Steel.** E. H. Lyons, jun. (Electrochemical Society, Oct., 1943, Preprint No. 84-12). The development of the electro-galvanising of steel strip in the United States is reviewed. Extremely uniform coatings of any desired weight which will stand severe forming can be deposited by this method. The cleaning process for the strip and the arrangement and operation of the plating tank are outlined. Objections to the Preece test and the salt-spray test are put forward, and the stripping test of the American Society for Testing Materials is recommended.

**Improved Chromating Process.** S. E. Maxon. (Steel, 1943, vol. 113, Dec. 13, pp. 134-136). A process for preventing the corrosion of zinc coatings on steel is described. This is known as "Cronak Chromating," and it comprises the immersion of the cleaned zinc-coated article for 5-20 sec. in a solution containing 200 g. of sodium dichromate and 6-9 c.c. of concentrated sulphuric acid per litre of water, followed by rinsing and drying.

**Rolling, Processing and Testing of Tinplate.** W. E. Hoare and E. S. Hedges. (Sheet Metal Industries, 1943, vol. 17, Jan., pp. 57-65, 67; Feb., pp. 239-242, 252; Mar., pp. 421-425, 438; Apr., pp. 605-610; May, pp. 791-799; June, pp. 975-978; July, pp. 1169-1176; Aug., pp. 1343-1347; Oct., pp. 1713-1722; Nov., pp. 1895-1899). A comprehensive and illustrated summary is presented of the various operations in the tinplate manufacturing process.

**Tin Plating from the Potassium Stannate Bath. Part II.** F. A. Lowenheim. (Electrochemical Society, Oct., 1943, Preprint No. 84-13). The advantages of the potassium stannate bath for tin-plating over the conventional stannate solution have already been outlined (*see Journ. I. and S.I.*, 1943, No. I., p. 93 A). In the present paper the effects of changes in bath composition upon the operating characteristics of the potassium stannate bath are reviewed and new data are supplied concerning the effect of the tin content on the anode efficiency. All the results reported are based on very thin deposits, as the work is directed to the application of the bath for the electro-tinning of steel strip.

**Electrolytic Tinplate from the Can Maker's Point of View.** K. W. Brighton. (Electrochemical Society, Oct., 1943, Preprint No. 84-18). Some of the characteristics of steel coated by the electrolytic process are reviewed. It is not practicable to produce hot-dip tin coatings lighter than 1.25 lb. per base box; at the present time electrolytic tinplate with only 0.5 lb. of tin per base box is being produced and, when enamelled, is quite satisfactory for packing many foods. The results of some corrosion tests on electrolytic tinplate are given.

**The Development of the Crucible Steel Electrolytic Tin Plate Process.** E. W. Hopper. (Electrochemical Society, Oct., 1943, Preprint No. 84-19). A brief description is given of the electrolytic tinning process developed by the Crucible Steel Co. of America.

The plating bath is made up of about 5 oz. of stannous sulphate per gal. and 5.75 oz. of sulphuric acid per gal. The anode and cathode current densities are normally about 50 amp. per sq. ft. For strip 20 in. wide and 0.0107 in. thick the plating speed is about 160 ft. per min. The tinned strip has a grey colour, and is subsequently scrubbed, dried and brightened. The brightening is done in a thermostatically controlled tank of hot oil held at about 235° F., the immersion time being 6 sec. The strip is next treated with cold oil, passed through squeegee rolls, degreased in trichlorethylene and wound into coils.

**Electrotinning and Its New Position.** F. A. Lowenheim. (*Metals and Alloys*, 1943, vol. 18, Oct., pp. 795-801). Data on the increased production of tinplate by the electrolytic process in the United States are given, and the relative merits of acid and alkaline electrolytes are discussed. In a given number of ampère-hours twice as much tin will be deposited by an acid bath as by an alkaline bath; furthermore, the current efficiency is usually higher in the case of the acid bath. Thus, higher production speeds are possible with acid baths. All acid solutions, however, require very close control of the organic addition agent to produce an acceptable deposit. Alkaline stannate solutions are extremely simple in composition, and will produce an acceptable deposit even if the composition is allowed to deviate widely from the optimum. The cleaning of the strip is much less of a problem with alkaline than with acid baths. Alkaline solutions have a better throwing power than acid solutions. In comparing sodium and potassium stannate baths it is found that the latter can be run at much higher cathode current densities than the former; the latter is also much less susceptible to hydrolysis, with the attendant precipitation of insoluble tin salts.

**Characteristics of Electric Apparatus Used on Electro-Tinning Lines.** G. E. Stoltz and W. G. Cook. (*Electrochemical Society*, Oct., 1943, Preprint 84-26). Three problems confronting the electrical engineer in charge of continuous electrolytic tinning plant are discussed—namely, the control of the current to the plating tanks, the control of the speed of the motors driving the strip through the tanks, and regulating the power supplied to the induction heating equipment for “flowing” the tin to suit the speed at which the strip is travelling. Special electrical apparatus to meet the particular requirements is recommended. In addition, a small photocell unit for detecting pinholes in tin coatings is described.

**Why Use Rectifiers for Plating?** L. W. Reinken. (*Metals and Alloys*, 1943, vol. 17, Mar., pp. 533-535). The advantages of rectifiers as compared with motor-generators for producing direct current for electroplating are discussed. The principal advantage of rectifier equipment is that individual units may be connected in parallel or series to obtain greater current capacity or higher voltage; any number of units may be interconnected without loss of efficiency or performance. The construction of rectifier equipment requires

only about 40% of the metals employed in a motor-generator of equivalent capacity, and, when finished, it occupies only about 10% of the floor space. The rectifier consumes less power than a motor-generator set of equivalent output because : (a) It can be started and stopped instantaneously so that it is easy to shut off between loads ; (b) its efficiency remains high at low loads ; and (c) by having separate rectifier units for plating tanks working at different voltages, there is no need to have separate tank rheostats which entail power losses.

**Industrial Electronics Helps Industry Break Production Records.** (Blast Furnace and Steel Plant, 1943, vol. 31, Nov., pp. 1258-1261, 1273). A brief report is presented of the proceedings at a conference of officials of the General Electric Company, on industrial electronics, which was held at Schenectady on September 14, 1943. Examples were given of the application of electronics for control purposes in a wide field of industrial operations, including the electrolytic deposition of metals.

**Select Right Instruments in Setting Up Automatically Controlled Plating Processes.** D. M. Nielsen. (Steel, 1943, vol. 113, Nov. 15, pp. 118-120, 160-162). Factors governing the selection of control instruments for plating baths are considered. For still plating baths with temperature control through pipe coils or electric resistance heating elements, it is almost universal practice to use "on-off" controllers. On some small plating baths the temperature is controlled by a water-jacket through which temperature-controlled water is circulated from a separate reservoir. If the reservoir is large and its temperature is controlled by the direct injection of steam or cold water, an on-off controller may be satisfactory. If the capacity is small and indirect heating through coils is used, a proportional controller may be needed.

**Tin Conservation in Britain.** J. Ireland. (Metals and Alloys, 1943, vol. 17, Feb., pp. 336-338; Mar., pp. 544-547). The measures taken in Great Britain to conserve tin fall into five divisions as follows : (1) Stopping the use of tin for unnecessary purposes ; (2) where tin is indispensable, devising means of using it more economically ; (3) the application of substitutes ; (4) the recovery of used tin ; and (5) stimulating home production. Where the toxic properties of lead do not matter, a lead-tin alloy is used in place of tin for plating steel sheet ; thus  $\frac{1}{2}$  lb. of tin plus  $1\frac{1}{2}$  lb. of lead per basis box is substituted for the usual  $1\frac{1}{2}$  lb. of tin. This new type of terne plate can be easily soldered, and makes good oil containers and gas-meter bodies. There were very few detinning plants in Britain ; the chief method in commercial use is the electrolytic stripping process using warm dilute caustic soda. At a South Wales plant the scrap is put into an autoclave and immersed in a solution of caustic soda, with sodium nitrate as an oxidising agent, at a pressure of 15 lb. per sq. in., and the stripping takes only about 30 min.

**Hot Dip Lead Coating Conserves Zinc.** W. Yonkman. (Steel, 1943, vol. 113, Nov. 15, pp. 127-130, 168). In order to conserve zinc in the United States, telephone pole fittings are now being lead-coated, and a hot-dip process by which this is done is the subject of the present paper. The sequence of operations is : (1) Oil is removed by any suitable means ; (2) rust and scale are removed in 6-12% sulphuric acid solution containing an inhibitor, at about 160° F. ; (3) immersion for 10-15 min. in a 5-10% hydro-chloric acid solution containing an inhibitor, at 120-150° F. ; (4) immersion in an aqueous solution of zinc ammonium chloride at room temperature until completely wetted ; and (5) dipping in molten lead at 690-710° F. No changes in the equipment are necessary when changing from hot-dip galvanising to hot-dip lead coating.

**The Use of Lead Alloy as a Substitute for Zinc in Coating Steel.** C. A. Kellogg. (Wire and Wire Products, 1943, vol. 18, Nov., pp. 714-715, 737). It is shown that a hot-dip galvanising plant can easily be adapted for lead-coating and some properties of lead coatings are discussed. The lead alloy coating (containing 95% min. of lead and 2.5% max. of tin) is considerably harder and stronger than lead ; it age-hardens in a very few days and becomes very resistant to abrasion. The alloy also acts as a lubricant in subsequent operations, such as forming, stamping and drawing.

**Radiant Gas Heat in Baking, Curing and Drying Operations.** C. P. Mann. (American Electroplaters' Society : Industrial Heating, 1943, vol. 10, Sept., pp. 1338-1342 ; Oct., pp. 1564-1570 ; Nov., pp. 1696-1703). The application of banks of gas-burners designed to supply radiant heat for the drying and baking of coatings on metal is discussed. Types of fuel, the design of burners and ovens, and the effects of the colour of the coating and its distance from the heat source are dealt with, several types of plant being described and illustrated.

## PROPERTIES AND TESTS

(Continued from pp. 134 A-137 A)

**Intercrystalline Cohesion of Metals.** E. R. Parker. (American Society for Metals, Oct., 1943, Preprint No. 8). Investigations and theories concerning high-temperature intercrystalline failures are reviewed. Transcrysalline fractures of metals may be produced at temperatures near the melting point by very rapid straining, whilst slow strain rates will cause intercrystalline fractures ; time is therefore a factor in high-temperature intercrystalline failures. As the mobility of atoms increases gradually with temperature, progressively longer times are necessary for intercrystalline failures

to occur as the temperature is lowered. Intercrystalline failures generally occur with less ductility than transcrystalline failures. The grain boundaries are a source of weakness at high temperatures and a source of strength at low temperatures. The modern concept of the crystal boundary structure is that there is a gradual transition across the boundary from one orientation to the other; the width of the crystal boundary is determined by the relative orientation of adjacent grains, being narrow for those having similar orientations, and wide for those differing the most.

**High-Yield-Stress Steel as Column and Beam Reinforcement.**  
C. E. Reynolds. (*Journal of the Institution of Civil Engineers*, 1944, vol. 21, Feb., pp. 227-250). The necessity for economising in steel in war-time encourages the use of high-strength steel bars for reinforcing concrete. The properties of high-yield-stress steels are examined with special reference to tests on twisted bars, and design problems relating to columns and beams are considered. Twisting a square bar causes deformation in planes originally parallel or normal to the bar axis. The major torsional overstrain in transverse planes is augmented by a small direct-stress overstrain. Within limits, the greater the degree of cold-working (measured by the number of twists) the higher are the yield and ultimate stresses and the less is the ductility. There is, for any given mild steel bar, a certain number of twists that gives a specified elongation, another that gives a specified yield stress, and a third that gives a specified ultimate stress. A specified maximum number of twists is essential to ensure that cold-working does not reduce the margin between initial failure and collapse by bringing the yield stress too close to the ultimate stress. An acceptable number of twists for square bars is a pitch of one complete twist on a length of 8-14 times the thickness. At normal temperatures the stabilising effects of cold-working last indefinitely, and prolonged heating at up to  $1300^{\circ}\text{ F}$ . has little effect; however, subjection for an hour or so to a temperature of  $1600^{\circ}\text{ F}$ . entirely removes the effect of cold-working.

**The Stress Distribution at the Neck of a Tension Specimen.**  
P. W. Bridgman. (*American Society for Metals*, Oct., 1943, Preprint No. 25). By approximating the contour at the neck of a tension specimen to a circle, and by using a circle to approximate the lines of the principal stress in the neighbourhood of the neck, the stress distribution across the neck has been found which rigorously satisfies the conditions of plasticity in the conventional form of von Mises. The same solution also applies with an error of only a few per cent when strain-hardening of a magnitude experienced in normal testing conditions occurs. The mathematical solution differs qualitatively from the stress distribution in an elastically strained specimen. In the plastically strained specimen the tension is greatest at the axis and least at the periphery; the stress system consists of an axial tension, uniform all the way

across the neck, plus a hydrostatic tension which is zero at the periphery and increases to a maximum at the axis. The effect of the variation of tension across the section is to make the mean tension higher than the true tension of flow. Numerical values and curves are given for converting one tension to the other.

#### The Diagnosis and Prevention of Failures in Colliery Wire Ropes.

A. E. McClelland. (*Proceedings of the South Wales Institute of Engineers*, 1944, vol. 59, No. 3, pp. 420-453). The main causes of breakage in colliery wire ropes are classified and the typical characteristics of each type of breakage are described. Much deterioration and some breakages would be avoided if the path of each rope were examined from time to time as the rope was running, with the object of noting and correcting all potential causes of deterioration, such as sharp bends, obstructions, water, slack rope and snatching. Many breakages could be avoided by careful examination of the whole exterior of the rope and of the interior of any lengths cut off during service; this affords a means of following the advance of deterioration. The person appointed to examine ropes at a colliery should be one who will take an interest in obtaining results and who will not regard the examinations as formalities. It is recommended that no rope should remain in service: (a) After it has lost 20% of its aggregate strength as a result of deterioration by wear or corrosion; (b) after it has lost 10% of its aggregate strength as a result of deterioration by fatigue, corrosion-fatigue, or surface embrittlement leading to fatigue; (c) after the outer wires have lost 40% of their thickness as a result of wear; and (d) after the outer wires have become loose and displaced for any reason.

#### Detecting Flaws in Sheets with Ultra-High Frequency Sound Waves.

A. Frost. (*Sheet Metal Industries*, 1944, vol. 19, Feb., pp. 255-257). **Intercrystalline Fracture in Sheets.** A. Frost. (*Zeitschrift des Vereins deutscher Ingenieure: Iron and Coal Trades Review*, 1944, vol. 148, Feb. 4, pp. 167-168). The difficulties encountered in the application of supersonics to the testing of steel plates for cracks are reviewed, and a new form of apparatus for carrying out such tests is described. In this the quartz oscillator of the transmitter is connected to a high-frequency current generator; the quartz is cemented to a metal block which transmits the mechanical oscillations of the quartz through water as the coupling fluid to the plate under test. A supersonic receiver on the opposite side of the plate is connected to an amplifier. When the waves from the transmitter meet an air cavity they are reflected and there is no response in the receiver; by moving the apparatus across the plate the position of cracks can be detected.

#### Some Experiments in Stress-Relieving Castings and Welded Structures by Vibration.

R. T. McGoldrick and H. E. Saunders. (*Journal of the American Society of Naval Engineers*, 1943, vol. 55, pp. 589-609). An account is given of experiments in the stress-relieving and stabilising of welded steel and cast-iron structures by

vibration and by a combination of vibration and annealing. The tests were carried out on : (a) Steel chair castings, 12 ft. long and 4 ft. long, used to support the heavy rails of towing carriage tracks, running along each side of a tank for making tests with model ships ; (b) a surface plate and lay-out table 12 ft.  $4\frac{1}{2}$  in.  $\times$  3 ft.  $7\frac{1}{2}$  in., weighing about 4 tons ; and (c) a box girder, 15 in.  $\times$  16 in.  $\times$  29 ft. 10 in. long, to carry a large towing dynamometer on a welded bridge structure running on the rails referred to in (a). After cleaning and rough-machining the chair castings, each one was either subjected to 25 heavy blows or to high-frequency vibration for 1 min. ; they were then annealed and, after cooling, vibrated as before. Castings stabilised in this way were checked at intervals of more than a year, and did not show any measurable change in shape. The surface plate was given similar treatment, but no precision check measurements have been made on it. The vibration test procedure on welded box girders was as follows : (1) To calculate the elastic constants of the box girders considered as simple beams ; (2) to estimate their natural frequencies when simply supported at the ends with the mass of the vibration generator added at the middle ; (3) to estimate the amplitude of vibration required to produce the selected stress range ; (4) to check experimentally the static stress produced by a deflection equal to this amplitude ; (5) to check experimentally the relation between dynamic stress and amplitude ; (6) to determine the form of resonance response of the girder and estimate the damping from this ; and (7) to vibrate the girder for 8 hr. or more at the required amplitude and frequency. No direct comparisons have been made between castings or structures treated by vibration and similar parts not so treated, but the satisfactory service given by these vibrated structures increases confidence in them and indicates that the treatment is worth while.

**Recent Developments in Mechanical Spring Design and Testing.**  
A. M. Wahl. (Wire and Wire Products, 1943, vol. 18, Nov., pp. 717-720, 735 ; Dec., pp. 778-780). The factors which should guide an engineer in the selection and design of springs are considered. The application of correction factors derived from Zimmerli's fatigue test data on small helical springs is explained and methods of calculating the stress in springs and their safe loads are discussed.

**Damping Capacity at Low Stresses in Light Alloys and Carbon Steel, with some Examples of Non-Destructive Testing.** L. Frommer and A. Murray. (Journal of the Institute of Metals, 1944, vol. 70, Jan., pp. 1-50). This work was undertaken to establish : (1) A reliable and accurate method for measuring the damping capacity of materials, particularly metals ; (2) the significance of the damping capacity as a physical property of the material in terms of other known characteristics ; (3) the influence exerted by structural defects, such as cracks and porosity, upon the measured damping, and thus to afford means for non-destructive testing ; and (4) the practicability of employing damping measurements as a means of quality control

and inspection of raw material and finished components. By careful design, and as the result of experiment, it has been found possible to separate excessive external damping losses from the intrinsic damping which it was desired to measure. It has been established that at room temperature the damping capacity of the principal aluminium alloys is of the order of  $10^{-5}$  as expressed by the logarithmic decrement. The measured damping is a constant up to a maximum shear stress of 30 lb. per sq. in. The damping of aluminium alloys appears to depend on the degree of precipitation present, being highest for maximum solid solution and lowest in the annealed state. The damping is markedly increased by small cracks or such porosity as would not normally occasion the rejection of a cast ingot. In some instances localised defects modify the damping at the various harmonics, so that the position of the defect can be estimated. This latter feature depends on the experimentally determined fact that the torsional damping does not vary over the available frequency range. The damping of a 0·6%-carbon steel has been studied up to a maximum stress of 90 lb. per sq. in., and has been found to be  $0\cdot5 \times 10^{-4}$  for the tempered condition and  $0\cdot7 \times 10^{-4}$  for the oil-quenched condition, these values being closely reproduced through successive cycles of heat treatment. Whilst the damping values found by this technique are comparable with those obtained by other workers employing a somewhat similar technique, they are many times smaller than those found at stresses a few times higher by the Föppl-Pertz technique (see Journ. I. and S.I., 1936, No. II., p. 393 F).

#### **The Influence of Lubricating-Oil Viscosity on Cylinder Wear.**

H. A. Everett. (S.A.E. Journal, 1943, vol. 51, May, pp. 165-169). A report on an investigation of the effect of the viscosity of the lubricating oil on the wear of cast-iron cylinders and piston rings is presented. Two groups, each of six single-cylinder engines, were run for 8-hr. periods. All conditions, except the viscosity, were artificially controlled to simulate the heavy-duty operation of motor buses, and each oil was tested in six engines for 8-hr. The wear was determined by evaluating the iron contamination of the crank-case oil and making adjustments for oil lost by consumption, leakage and sampling. Six oils covering a wide range of viscosity were used. The cylinder and ring wear decreased progressively with increasing viscosity throughout the range tested.

#### **Study Malleable Castings Properties for Military Applications.**

O. W. Simmons, P. C. Rosenthal and C. H. Lorig. (Foundry, 1943, vol. 71, Oct., pp. 102-104, 190; Nov., pp. 122-125, 190-192; Dec., pp. 107-108, 202-204). A report is presented of an investigation conducted by the War Metallurgy Committee at the request of the Office of Chief of Ordnance (U.S.A.) on the properties of malleable cast iron at temperatures ranging from  $-50^{\circ}\text{F}.$  to  $+1200^{\circ}\text{F}.$  Specimens of seven types of iron were subjected to tensile, tensile-impact, notched-bar-impact and wedge-bar-impact tests. The iron types

*A* and *B* had received the standard long-time malleabilising treatment; types *C* and *D* had received short-time treatment; type *G* was a cupola-produced iron containing total carbon 3.25%; types *E*, *F*, *H* and *P* were pearlitic malleable irons. The notched-bar-impact values all decreased as the temperature was reduced below 70° F. With unnotched bars the impact values were reduced only slightly at the low temperatures, except iron *G*, which showed a considerable reduction; the pearlitic irons *E* and *F* lost very little impact strength at low temperatures. At elevated temperatures the best combination of properties in all the irons was in the 75–200° F. range; at higher temperatures the ductility either remained constant or fell off up to about 600° F.; the Charpy impact values fell off continuously up to about 1000° F. The low-phosphorus short-time malleablised irons *C* and *D* had somewhat lower ductility than the irons *A* and *B* with normal phosphorus, although they followed the same trends with temperature changes.

**The Application Possibilities of Stainless and Heat-Resisting Steels Containing Nitrogen Additions.** F. Rapatz. (Iron and Steel Institute, 1944, Translation Series, No. 166). An English translation is presented of a paper which appeared in *Stahl und Eisen*, 1941, vol. 61, Nov. 27, pp. 1073–1078 (*see Journ. I. and S.I.*, 1942, No. I., p. 246 A).

**High-Manganese Stainless Steels.** D. J. Mack. (Metals and Alloys, 1943, vol. 18, Sept., pp. 507–512; Nov., pp. 1081–1084). A critical review is presented of the literature on the mechanical properties, corrosion-resistance, scaling-resistance, and creep of chromium-manganese and chromium-manganese-nickel stainless steels. The manganese stainless steels have excellent working, welding and fabricating properties, and it is believed that they are less susceptible to intergranular corrosion caused by carbide precipitation than are the chromium-nickel stainless steels; this is particularly true of welds.

**New Materials for Aircraft Engines.** M. Young and H. H. Hanink. (S.A.E. Journal, 1943, vol. 51, May, pp. 157–164). Data on the hardenability, machinability and special applications in aero engines of some of the NE chromium-nickel-molybdenum steels are presented and discussed.

**The Specification of Steel—By Analysis or Performance?** G. van Dyke. (Heat Treating and Forging, 1943, vol. 29, Nov., pp. 574–575, 591, 592). A scheme for specifying steels by analysis combined with a hardenability test is put forward. This paper appeared originally in Iron Age, 1943, vol. 152, Oct. 14, pp. 71–73 (*see p. 106 A*).

## CORROSION OF IRON AND STEEL

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(Continued from pp. 138 A-140 A)

**An Investigation of Substitute Materials for Packing Foodstuffs.** K. M. Edsäter. (*Teknisk Tidskrift*, 1944, vol. 74, Jan. 15, pp. 61-63). (In Swedish). The results of comparative corrosion tests on food cans made of black steel plate protected by one of the following coatings are presented : (1) One coat of sprayed lacquer ; (2) two coats of sprayed lacquer ; (3) phosphatised plus one coat of sprayed lacquer ; (4) phosphatised plus two coats of sprayed lacquer ; and (5) two coats of lacquer by dipping. The test solutions with which the cans were filled included distilled water, 1% common salt solution and water containing 10% of sugar and 0.5% of tartaric acid. Phosphatising did not increase the resistance to the sugar and tartaric acid solution. In other tests cans of lacquered black steel sheet were often more resistant to distilled water and salt solution than unlacquered tinplate. Rust formation was greatest in the tests with salt solution.

**Distribution of Galvanic Corrosion.** H. R. Copson. (*Electrochemical Society, Oct., 1943, Preprint No. 84-17*). The distribution of the galvanic corrosion of a nickel-to-steel couple in open, slowly moving, tap-water was estimated from measurements of potential differences in the water around the couple. The distribution was confirmed later by measurements of the decrease in thickness due to corrosion. The two methods were in excellent agreement. The maximum galvanic corrosion of the steel occurred at the junction of the two metals and decreased as the distance from the junction increased. The maximum effect at the junction was  $3\frac{1}{2}$  times the average galvanic corrosion. The normal uncoupled corrosion of the steel was greater than the average increased corrosion due to the galvanic effect despite the three-to-one area ratio of nickel to steel. Potential measurements can be made as soon as a steady state is reached, but it usually takes considerable time for corrosion to become extensive enough for thickness measurements to be accurate.

**Turbine Blade Deposits.** F. G. Straub. (*Midwest Power Conference, Chicago, 1943 : Iron and Steel*, 1944, vol. 17, Jan., pp. 224-225). The theories relating to the deposition of salts on turbine blades are considered. When silica is present in the boiler water, it may be in many forms or combinations. Thus, it may be combined with the NaOH as  $x\text{Na}_2\text{O} \cdot y\text{SiO}_2$ . From available data it appears that  $\text{SiO}_2$  is appreciably soluble in steam at a pressure of about 1500 lb. per sq. in. Apparently the silica occurs in the steam as  $x\text{Na}_2\text{O} \cdot y\text{SiO}_2$ , and forms on the turbine blades as the soluble sodium silicate, which is readily removed by washing. As the ratio of  $x$  to  $y$  decreases, the resulting salt has higher solubility and forms

lower down in the turbine, but in a form having lower solubility in water. Eventually a deposit will form which is almost pure silica. The data available relating to turbine blade deposits indicate that : (a) The insoluble silica deposits form in the 400–550° F. temperature range ; (b) the amount of silica deposited is not directly related to the soluble silica content of the boiler-water ; (c) it is possible that a proper balance of the chemicals in the boiler-water might reduce the silica deposits in the turbine.

**On the Effect of Chemical Composition of Alloy Steels upon Pit Corrosion in Aqueous Solution of Phenol.** P. Mikhalew, L. Zakharotchkine and N. Savitch. (*Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS*, 1942, vol. 34, No. 6, pp. 153–157). A report is presented of an investigation of the pitting corrosion of steels alloyed with : (a) chromium, (b) molybdenum and chromium, and (c) nickel and chromium in aqueous solutions of phenol. The specimens were immersed in the solution in test tubes and sealed, and then examined after periods of 12, 84, 452 and 552 hr. Ordinary carbon steel corroded uniformly over the whole surface. Increasing the chromium content increased the resistance to pitting corrosion. A 16/25 chromium-nickel steel began to show pits after 452 hr.; an 18/8 chromium-nickel steel had only four pits after 552 hr. Steels containing chromium 15% and 25% with molybdenum 2·64% and 3·72%, respectively, were practically immune from attack.

## BOOK NOTICE

(Continued from pp. 111 A–112 A)

BURNHAM, T. H., and G. O. HOSKINS. “*Iron and Steel in Britain 1870–1930.*” 8vo, pp. 352. London, 1943 : George Allen and Unwin, Ltd. (Price 25s.)

The object of this book is to explain why the British proportion of the world output of steel dropped from 43% in 1870 to 8% in 1930; and still more why the British share of the steel exports of the five leading countries dropped from over four-fifths to under one-fifth during the same period.

The factors responsible for this decline are divided into those which were beyond the iron and steel industry's control and those which were within its control. The “external” factors, to which perhaps most weight is given, are the high cost of transport, the export subsidies of competing countries and the low tax allowances for depreciation. Special factors in the last decade were the reconstruction of the Belgian and French industries with the assistance of Reparation payments, the depreciation of Continental currencies and the over-valuation of sterling, which simultaneously handicapped exports from and encouraged imports into this country. Other factors included the growth of protective tariffs, the lack of interest by British banks in long-term financing and the decline in the rate of foreign investment, although

the last-named was, it is argued, "a symptom rather than a cause of a weakness in British export industries."

The authors conclude, however, that the fact that some decline was inevitable does not account fully for its extent nor its direction or proportion, and that there were other factors for which the industry itself was responsible.

Their main criticisms are on familiar lines and can hardly be better indicated than by a few succinct quotations.

First, as regards coke : "There was, in fact, relatively to other countries, a definite lag in the erection of large centralized cokeries alongside blast-furnaces with full utilization of coke-oven gas and by-product recovery."

Next, pig iron : "Pig iron production was carried on in comparatively small blast-furnaces with low throughput and gross productivity per man . . . but large blast-furnaces were not only more efficient in operation but, suitably coupled with steel works of adequate capacity, would have given rise to savings in production costs, the most important of which was the overall fuel economy possible."

Thirdly, as regards steel-making and rolling : "Our competitors chose to install highly mechanized plants and maintain them at full output, and were justified by the results. If the British steel industry had developed the output of plants by modernization, specialization, integration and concentration of output, with the attendant fuel and labour economies, its competitive strength would have been considerably enhanced. After 1920 it had to face exceptional economic and financial difficulties and it was too late to put its house in order unaided."

Particular criticism is levelled at the delay in using East Midland ores : "The neglect of the Thomas process by Britain . . . is all the more surprising as for many years large and increasing quantities of basic Bessemer steel were being imported." "The irony of the position was that after going through the finishing processes this condemned class of steel was being sold as the best British products." "What was required was the setting up by 1890 of Thomas plants in Lincolnshire or Frodingham."

Next to come under fire are the re-rollers : "A number of firms were making small quantities of the same product, whereas the whole of the re-rollers could have been substituted by one or two large and efficient plants. In any case, the re-rollers ought to have co-operated to form a giant steel-making firm which could have supplied the large quantities of semi-finished steel they bought from abroad."

The industry's financial policy is criticised : "This lack of vision to accumulate reserves in the early part of the period for the modernization of plants, layouts and sites contributed to the almost insuperable difficulties with which the industry was confronted during the heavy depression in the twenties."

The final conclusion is that : "There is, in fact, good evidence to believe that the British iron and steel industry would not have declined relatively so fast or so far during the period reviewed had the men at the head possessed greater vision and a bolder and more energetic capacity for organization, direction and administration."

The authors have assembled a great deal of statistical information which at times makes their book rather heavy reading. They do, however, make a commendable effort to focus on the main issues by posing and endeavouring to answer leading questions, and by frequent summaries of their arguments.

There is a notable omission from the bibliography—namely, Mr. D. L. Burn's much fuller "Economic History of Steelmaking 1867-1939," published in 1940.

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## ORES—MINING AND TREATMENT

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(Continued from pp. 115 A-116 A)

**Bedding and Reclaiming Raw Materials.** A. J. Boynton. (*Iron and Steel Engineer*, 1944, vol. 21, Jan., pp. 66-74). A detailed description is given of the Robins-Messiter system of ore stocking. This is used for stocking iron ores from beds in which the physical properties and analysis of the ore vary considerably within comparatively short distances. The operation of bedding or stocking consists essentially in distributing material along one axis of a pile or bed, the distribution being made by a continuous reciprocating motion along this axis of a device for depositing the material at a constant rate. Reclaiming from the pile is effected by the removal of material on successive sections transverse to the bedding axis. The section may be vertical or inclined, the essential requirement being that it shall include an equal amount from each traverse of the depositing apparatus. A section thus reclaimed will contain the material necessary to constitute a sample of the pile, and, if sufficiently well mixed, it will be a representative sample of the entire pile. This enables ore of uniform composition to be continuously supplied to the blast-furnaces. An early plant of this type has been described in a paper on lean ores by W. A. Haven (*see Journ. I. and S.I.*, 1938, No. I., p. 309 A); some improvements and other systems of achieving the same object are described in the present paper.

**Concentration of Iron Ores in the United States.** T. B. Counselman. (*American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1629 : Mining Technology*, 1944, vol. 8, Jan.). A review is presented of methods of concentrating the Mesabi iron ores and the magnetites of the Eastern States.

**A Modern Sintering Plant.** (*Iron and Coal Trades Review*, 1944, vol. 148, Mar. 3, pp. 325-328). An illustrated description is given of a modern Dwight-Lloyd sintering machine and equipment at a blast-furnace plant in Great Britain. The sintering machine is a continuous belt, 125 ft. between drum centres providing 108 ft. run of effective sintering surface. The belt is built up of 134 pallets, 6 ft. wide by 2 ft. long, with a maximum depth of 13 in. The pallets are fitted with firebar bottoms. The belt travels normally at 8 ft. per min., at which speed the output is 1200 tons of sinter per 24 hr. when operating on raw material consisting of coke breeze 6%, scale 3%, flue dust 15% and fine ore 76%. The ignition fuel is cleaned blast-furnace gas. The time of ignition is 30 sec. and the total sintering time is 13½ min. The gas consumption is approximately 1828 cu. ft. per ton of sinter produced.

**Sintering of Iron Ore and Blast-Furnace Flue Dust; a Bibliography.** L. Filar. (*Blast Furnace and Steel Plant*, 1943, vol. 31, Nov., pp. 1262-1269). A bibliography covering the technical literature and the British and United States patents on the sintering of iron ore and blast-furnace flue dust is presented.

## REFRACTORY MATERIALS

(Continued from pp. 117 A-120 A)

**Recent Progress in the Manufacture of Refractories for Metallurgical Purposes.** Y. Letort. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, May, pp. 141-151; June, pp. 172-180; July, pp. 201-210). Progress in the manufacture of alumina, silica and magnesite refractories is reviewed and it is shown how X-ray technique and microscopical examination under polarised light have contributed to improving the properties of refractory bricks.

**Refractories as They Relate to the Steel Industry.** H. G. Fisk. (*Blast Furnace and Steel Plant*, 1943, vol. 31, Dec., pp. 1385-1390, 1424). The properties of fireclay, silica, basic and special refractories are discussed. At temperatures between 870° and 1470° C. quartz is transformed to tridymite in the presence of a flux. In a silica brick the lime acts as a flux to promote this transformation. Above 1470° C. cristobalite is the stable form of silica. Examination of silica bricks which have been in service in an open-hearth furnace roof shows that the silica mineral in the main body of the brick is tridymite, whereas the working surface of the brick consists largely of cristobalite. A recent development in the use of refractories derived from dolomite is to incorporate sufficient silica with the dolomite to combine with the lime and form calcium orthosilicate or tricalcium silicate, leaving the magnesia substantially uncombined in the form of periclase. At high temperatures silica combines preferentially with lime to form calcium silicates rather than with magnesia to form magnesium silicates, and the calcium silicates and periclase can coexist at furnace temperatures.

**Malleable Foundry Refractory Practice.** C. A. Brashares. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Dec., pp. 401-412). The refractories used in cupolas and in reverberatory, acid electric, Brackelsberg and acid open-hearth furnaces are discussed. With the trend towards higher operating temperatures it has been found economical to use super-duty fireclay bricks for the melting zone of cupolas. Hard-burned magnesite bricks are also being tried with some promise of success. Sand bottoms are still preferred for reverberatory furnaces used for cold charges; both super-duty fireclay bricks and 60% alumina

bricks are in use for bottoms when the furnace is used for hot metal charges. Brackelsberg furnaces are generally lined with silica brick backed with fireclay brick. In acid-lined electric furnaces, water-cooled angles in place of steel rings for supporting the skew-backs have been tried with success; with these, standard-size bricks or simple shapes can be adapted for the ring next to the angle. The acid open-hearth furnace for malleable iron production does not present any serious refractory problems; roofs lasting two years are normal, and a 9-in. roof is considered adequate.

**Refractory Cements.** J. H. Hartley. (*Steam Engineer*, 1944, vol. 13, Jan., pp. 99-101; Feb., pp. 153-155). The properties which a good refractory cement for boiler settings is required to have are discussed. Information on the behaviour of several types of refractories in boiler settings is given together with the chemical and mineralogical analyses of some of them. A recent development is the use of *Ciment Fondu*, which is an aluminous cement; although it can be used exactly like Portland cement, it differs entirely from it in its characteristics. It has slow initial set, extremely rapid hardening, high strength, immunity from sulphate attack and relatively high refractoriness. It is used as a bond for the production of refractory concrete and mortar. It is curious that a material so high in iron oxides and lime compounds should possess such satisfactory properties as a refractory bond.

## FUEL

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(Continued from pp. 143 A-145 A)

**Fuel and Metallurgical Furnaces.** R. Whitfield. (*Institute of Fuel: Iron and Steel*, 1944, vol. 17, Feb., pp. 269-274). Factors affecting the design and operation of metallurgical furnaces are considered. Data are presented and examples given showing: (a) The rapid increase in the rate of heat input required for small increases in the furnace temperature; (b) external heat losses through furnace walls; (c) heat loss by radiation when the furnace door is open; and (d) amount of cold air which is drawn into a furnace through badly fitting doors. Gas reactions in the furnace and factors influencing them are considered.

Producer gas and town gas are compared and the former is shown to be more advantageous. It is an open question whether recuperation is worth while when furnaces are worked intermittently, but on continuous furnaces recuperation always pays. The best design from a heat transfer point of view is that in which the flue gases travel slowly and the air quickly.

**An Australian Steel Works Power Plant.** L. Sanderson. (*Engineering and Boiler House Review*, 1944, vol. 58, Feb., pp. 47-48). A brief description of the boiler plant at the steelworks of Broken

Hill Proprietary Co., Ltd., in New South Wales is given. Steam is generated at four separate plants, all of which are placed near the point of steam utilisation. The blast-furnace boiler plant comprises fourteen water-tube boilers, six with a heating surface of 6182 sq. ft. each, that of the other eight being 5540 sq. ft. each. They are provided with Birkhulz-Terbeck burners for firing with blast-furnace gas. The A.C. power plant comprises four water-tube boilers with burners for blast-furnace gas. The main mill boiler plant contains twelve water-tube boilers equipped with chain-grate stokers, two burning coke breeze and two burning coal. The merchant mill boiler plant includes eleven boilers, each with 5540 sq. ft. of heating surface.

**Control of Sulfur and Ash in Mine-Run Metallurgical Coal, Report 1.** H. E. DeKay, L. A. Turnbull, J. N. Scudder and A. L. Toenges. (United States Bureau of Mines, Dec., 1943, Report of Investigations No. 3742). The methods and practices used to control the sulphur and ash contents in metallurgical coal at five mines are described. The descriptions are mainly confined to underground and surface operations before the coal passes to the cleaning plant. Maximum deviations of 0·007% and 0·03% from the average sulphur content in the raw coal and washed coal, respectively, are being obtained by a blending system at one mine where deviations of 0·15% used to occur frequently.

**Control of Powdered-Coal-Fired Melting Furnaces.** J. A. Durr. (Transactions of the American Foundrymen's Association, 1943, vol. 51, Dec., pp. 312-320). The principles of the combustion of pulverised coal are outlined and recommendations are made for controlling pulverised-coal-fired furnaces for making malleable cast iron. Good results are obtained with a coal 85% of which has passed through a 200-mesh sieve. A screw feed is better than a belt feed. The greatest efficiency is obtained with the burners set at 10° or 11° from the horizontal and the flame impinging on the furnace bottom 6 ft. 6 in. from the burners. A firing schedule should be adopted and adhered to. Regular inspections should be made to see that the coal-feeding mechanism is working properly and that the feed indicators are giving true readings.

**High-Pressure Coal-Briquetting Machine.** (Engineering, 1944, vol. 157, Feb. 25, pp. 146-147). An illustrated description is given of the Komarek-Greaves coal-briquetting machine. A binding agent is usually required for making coal briquettes, but in this machine the ground coal is compressed between indented rollers at a pressure of 30,000-40,000 lb. per sq. in.; no binder is required, and even low-volatile coal can be made into ellipsoidal briquettes sufficiently dense for transport and handling. The machine has rollers 23½ in. in dia. with a 13-in. face, and can produce 800 lb. of briquettes per hr. at 5 r.p.m.

**Control of Bulk Density of the Coal Charge in Byproduct Coke Ovens.** W. Seymour and L. D. Schmidt. (United States Bureau

of Mines, Dec., 1943, Report of Investigations No. 3743). One cause of non-uniformity of the coke produced by ordinary American coking practice is the prevailing lack of control of the bulk density of the coal charged in the ovens. The available information on the bulk density of crushed coal and its control is reviewed in the present report. If any plant receives all air-dried coal for a time, excessively high bulk densities causing dangerous expansion may result; this can be avoided by adding water to the dry coal. The effect of moisture is very pronounced, especially in the lower ranges; if the initial moisture is not too high an addition of water may make the bulk density more uniform. The use of oil for bulk-density control seems to be desirable. It decreases the density of dry coal and increases that of wet coal, and it can therefore be used to obtain more uniform density, regardless of the moisture content. The addition of oil is an easier method of control than that of greater additions of water. Additions of oil may increase production under certain conditions. A small amount of oil added to the coal at the mines lessens the difficulty of unloading trucks in frosty weather, diminishes the dust and causes the coal to flow more freely from hoppers. Crushing to a smaller size lowers the bulk density of coal except when it is air-dried.

**Correct Use of "Coking" and "Caking."** R. A. Mott. (Coke and Smokeless-Fuel Age, 1944, vol. 6, Feb., pp. 28-30). After a discussion of the meaning of the words "coking" and "caking" as applied in Great Britain, America and on the Continent, recommendations are made on the use of these and related terms. Broadly speaking, "caking" is now used to describe phenomena of powdered coal in a laboratory test, particularly the crucible test. Its application in Great Britain is so confusing that it should be abandoned altogether, and the terms "non-agglomerating," "agglomerating" and "poor, fair and strong swelling" be used to describe laboratory cokes. The terms "coking" and "non-coking" are most correctly applied to large-scale carbonisation practices. The terms "strongly-coking" and "weakly-coking" should be used only with discretion and a definition. The combustion engineer would probably find the terms "free-burning," "swelling" and "strongly-swelling" sufficient to describe the phenomena on a boiler grate.

**Some Physical Characteristics of By-Product Coke for Blast Furnaces.** C. C. Russell and M. Perch. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1943, vol. 154, pp. 116-134). The literature on the chemical and physical properties of American coking coals and coke, and the manner in which they affect coke-oven and blast-furnace operations is reviewed. The data presented are based on the A.S.T.M. standard methods of testing.

**Ash Structure in Coke.** L. Shnidman. (Industrial and Engineering Chemistry, Industrial Edition, 1943, vol. 35, Dec., pp. 1262-1263). A report of a study of the distribution and structure of

ash in a Pittsburgh coke is presented. Sections  $\frac{3}{16}$  in. thick were cut in different directions from lumps of coke ; these were placed on a lime asbestos board, photographed and heated slowly to 1300° F. in an electric furnace. After heating for 16 hr. the board was allowed to cool and the ash was photographed. The distribution of ash within a sample of coke is dependent on the presence of foreign matter and impurities, as well as on the coke structure. The combustible matter surrounds and envelops the ash residue. The volume of the ash residue is almost the same as that of the original coke sample. As the coal passes through the plastic state during the coking process there is no segregation of ash.

#### **Bases for the Increased Use of Blast-Furnace Gas in Ironworks.**

A. Schack. (Iron and Steel Institute, 1944, Translation Series, No. 168). An English translation is presented of a paper which appeared in Stahl und Eisen, 1938, vol. 58, Feb. 17, pp. 157-163 (see Journ. I. and S.I., 1938, No. I., p. 306 A).

**Modern Metallurgical Gas Producers.** F. Reddet. (Revue de Métallurgie, Mémoires, 1942, vol. 39, May, pp. 129-140). A detailed description is given of a modern water-jacketed gas producer with auxiliary gas-cleaning equipment. Particular attention is paid to the fittings for automatic continuous operation. The data obtained in acceptance tests for another producer are presented and discussed.

**Gas Cleaning.** (Iron and Steel, 1944, vol. 17, Feb., pp. 247-249). Operating data for single- and two-stage electro-precipitators for cleaning blast-furnace gas are discussed and compared. The influence of various factors governing precipitator efficiency has been investigated at length. For blast-furnace gas, tower cooling to 70-90° C. is required, or the dew point of the raw gas must be raised accordingly. For some plants of the dry precipitator type, operating temperatures as high as 250-300° C. are reported, but in these cases dust contents of 0.088-0.22 grains per cu. ft. at N.T.P. have had to be tolerated. In the two-stage process the gas passes through a wet precipitator after the dry one ; this plant meets the demand for a dust content not exceeding 0.002 grains per cu. ft. and a clean gas temperature of 20-25° C. With this type of plant, 85-95% of the dust is removed in the dry state in the first stage, which means a low water consumption and reduces the size of the slurry thickening plant. The power consumption of the two-stage system is usually in the range of 0.017-0.023 kWh. per 1000 cu. ft. of gas treated, to which must be added about 0.0285 kWh. per 1000 cu. ft. for water circulation. The gas pressure drop through the plant is between 2.3 and 3.5 in. of water. With the object of reducing the capital cost of the plant, a single-stage wet process has been developed ; with this, the dust content of the cleaned gas is 0.002-0.0045 grains per cu. ft., the power consumption of the precipitator is 0.0115 to 0.017 kWh. per 1000 cu. ft., the total consumption for the complete plant is 0.048-0.054

kWh. and the drop in the gas pressure is only 1.5-2.5 in. of water. The capital cost is about 30% less than that of the two-stage plant, but the water consumption of the former is about 50% greater than that of the latter.

**Hydrogenation and Liquefaction of Coal. Part IV.—Effect of Temperature, Catalyst and Rank of Coal on Rates of Coal-Hydrogenation Reactions.** H. H. Storch, C. H. Fisher, C. O. Hawk and A. Eisner. (United States Bureau of Mines, 1943, Technical Paper No. 654).

**Colloidal Oil as a War and Post-War Fuel.** J. G. Coutant. (Iron and Steel Engineer, 1944, vol. 21, Jan., pp. 58-64). Data on the estimated cost of manufacturing "colloidal oil," which is a composite fuel consisting of fuel oil 60% and coal (in colloid form) 40%, are presented and its heating value and cost are related to those of fuel oil alone. Details of a mill into which the oil and ground coal mixture is fed to be reduced to a colloidal suspension are given, together with a scheme for a plant to produce 600,000 barrels per year. The use of this fuel under boilers offers considerable economic advantages and is receiving special attention by the fuel authorities in the United States. This paper supplements the information given in an earlier one (see p. 145 A).

## PRODUCTION OF IRON

(Continued from pp. 145 A-147 A)

**Defense Plant Corporation Blast Furnace Blown-In at Republic Steel Plant.** (Blast Furnace and Steel Plant, 1943, vol. 31, Dec., pp. 1373-1375). Brief particulars are given of the new No. 5 blast-furnace which was blown in on October 28, 1943, at the works of the Republic Steel Corporation. It is 105 ft. 6 in. high, with a hearth diameter of 27 ft. and has eighteen tuyeres. The average production will be five casts of 260 tons each per day. The plant includes an ore unloading dock, ore and limestone storage yard, pumping station, pig casting machine and a battery of 75 coke-ovens with a by-product and benzol plant.

**Essential Considerations in the Design of Blast Furnaces.** A. L. Foell. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1943, vol. 154, pp. 43-61). Improvements in blast-furnace design in the United States, with special reference to equipment at the furnace top, are reviewed and discussed. The furnace top above the top platform includes the gas-recovery system in the form of uptakes, bleeder stacks and downcomers, and the filling equipment, the last-named consisting of the revolving distributor, receiving hopper, bell beams or bell operator, skip sheaves and the dumping portion of the skip bridge. In the three

types of top arrangement most common in the United States, the uptakes, bleeder stacks and downcomers are directly supported either by the furnace shell or top platform, and the distributor and revolving hopper by the furnace top ring. On recently built furnaces the top charging mechanism is supported either by a structure carried on the bleeder stacks or by an independent structure separately supported on the top platform; the latter is the better arrangement. Diagrams of these structures are presented. In the stockhouse, hand-operated bin gates are considered better than mechanically operated gates. Many furnaces are equipped with rheostatically controlled drives for the skip hoist, but the present trend is towards double-motor, double-generator, variable voltage drives. The installation of larger hot-blast valves, trunks and mains to handle the greater volumes of blast for large furnaces has caused a system of blast mixing to be applied in which the mixing air is introduced at each stove into the lower part of the hot-blast trunk, where complete mixing is accomplished before the air reaches the hot-blast main. By thus limiting the temperatures in all parts of the hot-blast system to the temperature demanded by the furnace, obvious advantages are obtained. In most cases this temperature is well below 1400° F.; stratification is eliminated and the hot-blast system is protected from sudden temperature changes. The additional cost of this system is not high. Gas-cleaning equipment is also discussed.

**Calcination Rates and Sizing of Blast-Furnace Flux.** T. L. Joseph, H. M. Beatty and G. Bitsianes. (*Transactions of the American Institute of Mining and Metallurgical Engineers*, 1943, vol. 154, pp. 148-161). Comparative tests on a wide variety of fluxes ranging from dolomite to high-calcium limestones disclosed that some calcined about three times as fast as others. The more porous stones were, in general, higher in magnesia and calcined at faster rates. High-calcium limestones calcined at the slowest rate, dolomitic limestones at intermediate rates and dolomites at the most rapid rate, but unusually porous limestones and exceptionally dense dolomites calcined at intermediate rates. Differences observed in the rates of calcination of high-calcium stone cannot be accounted for by comparatively small differences in porosity and magnesia content. Up to about 50% calcination, the rate of evolution of carbon dioxide is closely related to the amount of magnesia in dolomitic limestone and dolomites. This may be due to the decomposition of magnesium carbonate throughout the specimen in the early stages rather than in a definite or restricted zone of calcination. Until a more definite relation is established between physical properties, composition and rates of calcination, comparative tests will be necessary to obtain accurate information. By conducting such tests at a fixed temperature accurate comparisons can be made. In order to apply the results of laboratory tests to the sizing of blast-furnace flux, a study was made of the

time the stock remains in different temperature zones when the distance from the stock line to the top of the bosh varies from 50 to 70 ft. Calcination that begins at about 800° C. should be completed at below 1050° C. to avoid solution loss. In taller furnaces, the stock remains in this temperature zone for a longer time, thus permitting complete calcination of larger pieces. The results indicate that high-calcium stone should be crushed to from 3 to 4 in., dolomitic limestone to from 4 to 6 in. and porous dolomites to from 6 to 8 in., the exact size depending on the furnace height. Although larger pieces of material higher in magnesia can be calcined before solution loss occurs, smaller sizes would be more effective in promoting the permeability of denser portions of the stock column.

**Anthracite Pig Iron.** R. H. Sweetser. (*Iron Age*, 1943, vol. 152, Dec. 30, pp. 32-39). The history of the operation of blast-furnaces with anthracite in the United States is reviewed. From 1855 to 1875 anthracite was the prevailing blast-furnace fuel. It was widely believed that it was necessary to cut down the tuyere area, and this led to a decrease in the production when a change-over from charcoal to anthracite was made in the same furnace. The use of anthracite alone was confined to a comparatively short period, for it soon became the practice to mix coke with it. Whether Pennsylvanian anthracite will again be used as a blast-furnace fuel depends on two unpredictable factors—namely, the attitude of the personnel of the anthracite industry whose research work does not include the reduction of iron ores, and the comparative costs of egg-size anthracite and coke.

**The Sulphur in Pig Iron.** M. Grison. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, Jan., pp. 1-11). After a review of the literature on the theory and advantages and disadvantages of desulphurising molten iron with sodium carbonate, details are given of the results of trials carried out at blast-furnaces in the Longwy district in France during 1939 and 1940. The first trial was made by stopping the use of manganese-bearing additions and open-hearth slags to one blast-furnace burden and putting the iron produced in a mixer together with the product of a normally burdened blast-furnace. The iron from the mixer contained 0.80% of manganese; this was made into steel, and the rolled products were quite satisfactory. In the second trial the sulphur content was lowered by sodium carbonate at the blast-furnace taphole from 0.203% to 0.079%, using 9.08 kg. of carbonate per ton (1000 kg.) of iron; the lime/silica ratio of the slag was 1.26. The regular practice of desulphurising with sodium carbonate and working with a lime/silica ratio of about 1.3 was then adopted at all three furnaces at this works. To prolong the life of the lining of a new 1000-ton mixer, desulphurising was carried out at the mixer spout, and only in the exceptional cases, when the sulphur in the iron leaving the blast-furnace exceeded 0.250%, was de-

sulphurising done before the mixer. The saving in the cost of manganese-bearing ores greatly exceeded the expenditure on sodium carbonate.

**Ferro-Silicon Production.** (Electrical Review, 1944, vol. 134, Jan. 7, pp. 3-8). A description is given of a large electric arc furnace for smelting silica rock, coke and steel turnings to produce ferro-silicon. The furnace has a hearth 20 ft. in dia. and the height of the melting chamber is 10 ft. The electrical load is about 10,000 kVA. Because of the continuous operation, with no breaks for charging, sections of the electrodes are continuously fitted into guides above the furnace and fed downwards as they are consumed at the bottom. Each electrode is  $41\frac{1}{4}$  in. in dia. and weighs about 16 tons, so that very special equipment has had to be designed to support and control their movement; this equipment is described and illustrated.

**Production of Low-Sulphur Sponge Iron.** R. C. Buehl and E. P. Shoub. (Mining and Metallurgy, 1943, vol. 24, Dec., p. 550). A short account is given of tests by the United States Bureau of Mines on the production of low-sulphur sponge iron in an internally-fired rotary kiln making about  $1\frac{1}{2}$  tons of iron per day. Coke from a Pittsburgh coal containing 0·9% of sulphur was crushed and intimately mixed with powdered limestone in the proportion of five parts of coal to one of limestone. A New York State magnetite ore was successfully reduced with this "lime coke" to produce a sponge iron containing 0·04-0·07% of sulphur.

**Powder Metallurgy.** W. D. Jones. (Journal of the Institution of Production Engineers, 1944, vol. 23, Feb., pp. 35-52). The principles of powder metallurgy are explained and the typical physical properties of the products are indicated. Automobile parts made from ferrous metal powders include thrust washers, fan bearings, oil-pump gears, levers, cams, bearing retainers and instrument parts. Commercially produced iron parts have a tensile strength of 15,000-35,000 lb. per sq. in. with either no ductility or an elongation of less than 5%. There will soon be no difficulty in making parts with a cheap iron powder which will have over 20 tons per sq. in. tensile strength, but no appreciable elongation. Recommendations for training staff and for experimental work with a view to manufacturing parts by the process are made.

## FOUNDRY PRACTICE

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(Continued from pp. 147 A-149 A)

**Heat-Treating Cast Iron.** J. Edmiston. (Metallurgia, 1944, vol. 29, Jan., pp. 138-140). The principles upon which the founding and heat treatment of high-duty cast irons are based are discussed.

Low total-carbon irons are readily melted in the cupola with suitable steel and pig-iron charges, and superheating can be applied for grain refinement to produce the nodular graphite desired in high-duty iron; before pouring into moulds, however, the metal is cooled off in the ladle to a suitable casting temperature. This procedure is difficult with small castings, but progress has been made with acid-lined arc furnaces of small capacity for this type of foundry. With total carbon under control, the combined carbon in the casting depends on the amount of graphitising element present. For small to medium engineering castings, 1·75–2·5% of silicon is required and the sulphur should be limited to 0·15%, with sufficient manganese (about eight times the sulphur content) to cover the weakening effect of the sulphur. For pressure-tight castings of simple design, phosphorus should be limited to 0·1%, rising perhaps to 0·15–0·2% for more intricate shapes. The specification suggested for a plain carbon high-duty iron is : Total carbon 2·9–3·5%, combined carbon 0·6–0·8%, silicon 1·7–2·5%, sulphur 0·1% max., phosphorus 0·1–0·4% and manganese 0·6–0·9%. Such an iron with controlled graphite formation could be oil-quenched from 850° C. to give a surface hardness of not less than 400 Vicker's diamond pyramid in sections up to about  $\frac{1}{2}$  in.

**Cupola/Electric-Furnace Duplexing of Malleable Iron.** C. Morrison. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Dec., pp. 277–307). The cupola/electric-furnace duplex process of producing malleable cast iron at the Saginaw Works of the General Motors Corporation is described. Melting is done in four 78-in. inside dia. cupolas, two being used at a time. Each cupola has a 10-ton tilting fore-hearth with a teapot spout. Desulphurising is done in the fore-hearth. Two electric furnaces are used for refining and superheating. When 3 tons of metal have been taken from the electric furnace this is replaced by metal from the fore-hearth. About 250 lb. of hydraulically compressed steel scrap are charged in the electric furnace with each 3 tons of cupola metal. Charts have been prepared from which the blast requirements to produce any desired melting rate for a given amount of fixed carbon in the coke can be read off and the humidity calculated. The humidity is controlled at about 4·2 grains of moisture per cu. ft. of blast. The blast is heated by gas-fired heat exchangers to about 300° F. and a temperature recorder is used. Iron made with hot blast is more easily malleabilised than that made with cold blast, and trouble with heavy, viscous slags is practically eliminated when using heated blast, but it is necessary to provide water-cooling to the bosh shell-plate. The amount of graphitic carbon in all the materials charged is known at all times, and the annealed malleable cast iron scrap is weighed separately from the hard iron sprues. The chemical change in the iron in the electric furnace is slight, but the physical change is considerable. The electric furnaces are operated with the doors open at all times, for,

with the doors closed, the iron easily becomes mottled on casting; this phenomenon is not clearly understood, but experience has shown that deoxidising conditions promote the formation of primary graphite. Test sprues are poured every 20 min. from each electric furnace; these are 7 in. long and taper from 2 in. to  $1\frac{1}{2}$  in. in dia.; they are cast in green sand, allowed to cool slowly until black, quenched in water and broken; the amount of steel which should be added is largely determined from the appearance of the fracture. Sets of bars  $\frac{1}{2}$  in. sq.  $\times$  7 in. long are cast every 30 min. and a series representing the day's work is passed through the malleablising kiln; these are fractured and examined for any irregularities.

**Melting Malleable Iron with Oil in the Air Furnace.** A. Van Lantschoot. (Transactions of the American Foundrymen's Association, 1943, vol. 51, Dec., pp. 343-360). A brief description is given of an oil-fired furnace with a hearth 22 ft.  $\times$  6 ft. for melting iron for malleablising. A combustion chamber 9 ft. long gives the best results with the mixing burner used; the mouth of the combustion chamber is 18 in. narrower than the hearth. When the furnace bottom is lowered to accommodate larger heats, the rear bridge wall is lowered also. The stack is 3 ft. in inside dia. and only 50 ft. high and has a checker opening to prolong the life of the stack lining and to reduce the draft, as only a slight draft is required for oil burning. The oil is preheated to about 130° F. and is atomised by a jet of steam at 40-50 lb. per sq. in. Heats ranging from 13 to 16 tons are melted with 170 gal. of oil per hr. and 4700 cu. ft. of air per min. Secondary air is admitted through openings only 4 in. apart across the entire width of the combustion chamber. Some particulars of the charging and melting practice and of the properties of the iron produced are given.

**Melting Cupola Malleable Iron.** H. W. Maack. (Transactions of the American Foundrymen's Association, 1943, vol. 51, Dec., pp. 377-385). A brief account of cupola practice in the United States for producing iron for malleablising is given. The standard form of cupola is used with a hearth depth of about 18 in. A coke-bed extending about 50 in. above the tuyeres is about right for a cupola operated at 16-20 oz. blast pressure. Foundry returns may comprise 40-50% of the charge, and the average carbon content of the metal charge is about 2.25%. The essential difference between cupola and reverberatory furnace malleable iron is the higher percentage of carbon in the former; the proportions of manganese and sulphur are also higher, but, when these are kept in the proper relationship, the physical properties of the iron are not affected.

**Practical Operating Phases of Melting.** J. H. Lansing. (Transactions of the American Foundrymen's Association, 1943, vol. 51, Dec., pp. 387-400). The advantages and disadvantages of reverberatory, open-hearth, Brackelsberg and electric furnaces, as

well as various duplex processes, for producing malleable cast iron are briefly reviewed.

**Present Status of the Side-Blow Converter.** A. W. Gregg and F. B. Skeates. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Dec., pp. 504-514). Some developments in America in the use of the Tropenas converter for producing steel for castings are reviewed. The use of photo-electric cell units to determine the end-point of the carbon blow has resulted in better control and more uniform production at many foundries; so also has the regulation of blast pressure during the blow by remote control from the operator's pulpit. The Yocom method of dephosphorising is working well at one foundry; this consists of a ladle treatment of the metal with a mixture of calcium oxide, iron oxide and fluorspar. The Ford Motor Company has experimented with a basic-lined cupola for removing the phosphorus, and the results are promising. The results of investigations by C. E. Sims and F. B. Dahle on the properties of cast steel made by six different processes are quoted (*see Journ. I. and S.I.*, 1943, No. I., p. 60 A).

**Study and Practical Application of a Special Electric-Furnace Nickel-Manganese-Molybdenum Steel for Castings.** J. Cournot. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, Feb., pp. 61-64). A description is given of the electric furnace melting and refining procedure which was developed at a French works to produce steel suitable for making castings 2 m. long of very irregular shape, the thickness varying between 8 and 40 mm., weighing about 750 kg., with a tensile strength of at least 70 kg. per sq. mm. and 11% elongation. Having regard to the raw material situation in France, the composition finally selected was carbon 0.25%, nickel 2.10%, manganese 1.00%, molybdenum 0.30% and silicon 0.37%. The castings were poured in ordinary steel-foundry sand without difficulty. They were annealed for 4 hr. at 1025° C. and normalised twice, once from 910° C. and the second time from 875° C., with a final grain-refining treatment of 1-2 hr. at between 570° and 610° C.

**The Use of Wood Dust in Moulding Sand.** (*Institute of British Foundrymen*, Dec., 1943). This is a report of the Sands Sub-Committee of the Technical Committee of the Institute of British Foundrymen on an investigation of the use of wood dust as a substitute for coal dust in naturally bonded sand and in synthetic green sand. Wood dust of suitable type can be used as a substitute for coal dust for most light and medium-weight iron castings. The amount of wood dust required is approximately one-fourth the weight of coal dust used for the same sand mixture; this is based on the relative percentage of volatile matter in the two materials. Wood dust reduces the green compression strength of the sand mixture by about 15%. The plasticity or deformation of the sand is increased by the addition of wood dust. With

continued use the rate of deterioration of the sand is reduced and economy in new sand should follow.

**Hand Grenades Made of Gray Cast Iron.** E. Bremer. (Foundry, 1943, vol. 71, Dec., pp. 104-105, 184, 185). A brief description is given of the mould- and core-making technique for casting hand grenades in grey iron at the foundry of the Dunkirk Radiator Corporation, Dunkirk, New York State.

**Precision Casting.** (Steel, 1944, vol. 114, Jan. 10, pp. 78-82, 96). Some particulars are given of the extension of casting methods used by dentists and jewellers to the production of castings in alloy steels, tool steels and bronze weighing up to 7 lb. The process is sometimes called the "lost wax" method, because the pattern is made of wax or a plastic which can be melted or vaporised away without leaving any residue. Providing the correct moulding materials are selected and the proper technique is applied, castings can be produced in some alloys to within less than 0·001 in. of the required dimensions. The actual casting is made by the centrifugal, pressure or vacuum method. In the pressure process a totally enclosed indirect-arc furnace mounted on trunnions and capable of being inverted is used. The mould assembly is placed upside down on top of the furnace and clamped in position so that the furnace taphole and the mould entry coincide. The whole apparatus is inverted when the metal is ready for casting.

**Casting Spinning Practice.** (Iron Age, 1943, vol. 152, Dec. 2, pp. 54-59). An illustrated description is given of the practice adopted by the Ford Motor Company of Canada, Ltd., for the centrifugal casting of knuckle joints, sprockets, tank-track pins, brake shoes and other steel parts for war purposes. A "splash core" is placed in the metal moulds for the knuckle joints; this is positioned so that it protects the mould surface from erosion by the stream of steel entering the mould. A large turntable with twelve mould spinners is employed; as each mould is moved by this table to the pouring area, a limit switch is actuated which sets the mould spinning at 170 r.p.m. This arrangement facilitates pouring at the rate of 100 moulds per hr. There are also eight independent vertical spinning tables for flasks up to 23 in. in dia.

## PRODUCTION OF STEEL

(Continued from pp. 149 A-150 A)

**Developments in the Iron and Steel Industry during 1943.** (Iron and Steel Engineer, 1944, vol. 21, Jan., pp. 79-92). A review of the increase in the production of the iron and steel industry of the United States in 1943 and how it was achieved is presented. Pig-iron production increased from 59 million tons in 1942 to 61 million

tons in 1943. A total of twenty-two sintering plants are either under construction or have been completed. Steel production in open-hearth furnaces amounted to  $78\frac{1}{2}$  million tons in 1943. The use of high-magnesia ramming mixtures for basic open-hearth and electric furnace bottoms has increased greatly; the time required to prepare a bottom with this material is only about a quarter of that required for burning in a bottom. Electric furnace steel-making capacity has increased from  $4\frac{1}{2}$  to 6 million tons in the course of 1943. Several works have installed briquetting machines for steel turnings. A number of rotary hearth furnaces with capacities up to 10–12 tons per hr. have been applied to heating billets for forging, pressing and upsetting. Equipment for rolling, tinning, oxy-acetylene cutting, conveying materials and electrical developments are included in the review.

**The Statistical Position of the Steel Industry.** (Steel, 1944, vol. 114, Jan. 3, pp. 206–213). Tables are presented which show the quantities of pig-iron, coke and steel which the different makers in the United States will be able to produce on completion of the plant expansion programme in 1944. Details of new iron-ore mines, new electrolytic tinplate lines and the expansion programmes for rolling-mill and ore-sintering plants are also given.

**Open-Hearth Furnaces in France.** P. Bertrand and E. Dupuy. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, June, pp. 161–171; July, pp. 193–200). The methods of operating open-hearth furnaces in France, with particular reference to the consumption of fuel and refractories in relation to output, are discussed. The geographical situation of the various works in France has an important effect on the steelmaking economy. It is recommended that open-hearth furnaces with their gas producers should be studied as a unit, and in particular, that investigations of the following items should be made at carefully selected works: (1) The composition and calorific value of the producer gas and any changes in its properties between the gas in the producer and the gas at the furnace ports; (2) changes in the composition of the waste gas as it passes from the furnace to the stack; (3) changes in fuel consumption during a heat; (4) changes in temperature, pressure and rate of flow of the gas entering and leaving the furnace.

**The Relative Deoxidising Power of Boron in Liquid Steel and the Elimination of Boron in the Open-Hearth Process.** R. W. Gurry. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1641: *Metals Technology*, 1943, vol. 10, Dec.). A method of calculating the deoxidising power of boron in liquid steel is explained, and it is shown that its deoxidising power is greater than that of silicon, vanadium and titanium, and approaches that of zirconium and aluminium. The relatively high affinity of boron for oxygen indicates that, if no more powerful deoxidising agent is present, boron would oxidise out during teeming. If the boron is introduced as ferro-boron to increase the

hardenability, the steel should first be deoxidised with aluminium or some other very powerful agent.

**Hardness Measurements as a Rapid Means for Determining Carbon Content of Carbon and Low-Alloy Steels.** K. L. Clark and N. Kowall. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1681 : Metals Technology, 1944, vol. 11, Jan.). A technique is described for casting small chilled samples of steel, taking hardness readings and determining the carbon content from a previously determined curve relating the as-quenched hardness to the carbon content. A split mould  $3\frac{1}{2}$  in. long  $\times 1\frac{1}{2}$  in. outside dia. with a cavity  $\frac{3}{4}$  in. in dia. at the top ending in a cylindrical portion 1 in. long  $\times \frac{1}{4}$  in. in dia. is used. The sample is quenched in ice-water, and cuts about  $\frac{1}{4}$  in. apart are made with a water-cooled abrasive wheel across the narrow portion. Rockwell hardness readings are then made at points on the section  $\frac{1}{8}$  in. from the centre. The entire procedure takes about 2 min. The results are reproducible and sufficiently accurate for steel-making control purposes. Unskilled personnel can easily be trained to perform the test.

**Some Notes on Slags and Slag Control in Basic Open-Hearth Tilting Furnaces Using Phosphoric Iron.** A. Jackson. (Iron and Steel Institute, 1944, this Journal, Section I). The notes illustrate the chronological development of a slag control method, designed first for use during refining, but subsequently enlarged to embody also the charging of lime in furnaces using high percentages of molten phosphoric iron. Commencing with a brief general résumé of the process, the paper shows the variable nature of the iron used and a series of tapping-slag analyses, illustrating a ratio between the total slag iron and the slag acids, silica plus phosphoric acid. From this follows the development of slag control for refining. Next the method of estimating and adding the limestone for charging is described, followed by three series of slag analyses taken just before removing the primary slag, from the primary slag and from the slag during tapping. The relationship between the slag and metal composition is indicated and graphs are plotted. It is also shown that the slag iron varies throughout refining with the iron in the primary slag before removal, which effect, though somewhat reduced towards tapping, is still appreciable. These slag irons vary within limits with the silicon in the mixer iron charged, and tend to support the previous impression that changes in the composition of the blast-furnace iron are reflected in the properties of the finished steel.

The mean analyses of a large number of slags are presented, from which numerous relationships can be developed, the most interesting probably being the inverse type of ratio between the silica plus phosphoric acid and the total iron, or iron oxides, with relatively constant lime. This tends to suggest that iron oxides may replace silica and phosphoric acid in the silico-phosphates

of lime normally present in slags of this type, or that they associate in relatively definite quantities with any lime present which is not in combination with silica and phosphoric acid. The conclusions point to some increased production resulting from the application of the methods outlined, but in particular indicate slag control to be one more step towards attaining uniformity of operation and product in the basic open-hearth. The developments used for the manufacture of other than ordinary boiler plate and section steels are not described in these notes.

**Rotating Regulator for Arc Furnaces.** R. A. Geiselman, C. C. Levy and W. R. Harris. (*Electrical Engineering*, 1943, vol. 62, Nov., pp. 671-674). A description is given of the Rototrol regulator for controlling the current to the motor which moves the electrodes of electric-arc steel furnaces. This regulator is essentially a small set generating direct current for the electrode motor. The magnetic circuit of the generator is excited by a number of field windings. As the charge melts and flows away, and as the electrodes burn off, the balance between the control fields is continuously disturbed and the Rototrol changes the generator voltage to move the electrodes to maintain the balance between arc voltage and current. Examples of the performance of a typical installation are given, and these show that the electrode motor speed responds rapidly to changes in the arc voltage.

**Progress in Supplying Power to Arc Furnaces.** C. C. Levy. (*Iron and Steel Engineer*, 1944, vol. 21, Jan., pp. 36-42). Feeder and control circuits for electric-arc steel furnaces are described and discussed. Power factor correction for furnace circuits is obtained by synchronous condensers or by shunt-connected static capacitors. The synchronous condenser has the advantage that it offers improvement in line regulation and some decrease in voltage flicker. The shunt-connected static capacitor has a lower first cost and low maintenance to recommend it, and it is to be preferred for small installations. Recent installations have incorporated "demand metering" and associated equipment to keep the load within specified maximum demand limits; this equipment includes an alarm signal to the operator so that he can reduce the furnace load or means of automatically tripping the circuit breaker on one or more of the furnaces. Rotating regulators for arc furnaces are also considered (see preceding abstract).

**A New Method of Casting Steel Ingots or Blocks.** P. F. Erichsen. (*Zeitschrift des Vereines Deutscher Ingenieure*: *Mechanical World*, 1944, vol. 115, Jan. 28, p. 95). Some experiments in the casting of non-ferrous metal and steel ingots in special moulds with the object of eliminating pipe and producing almost "ideal" ingots are described. A water-cooled horizontal chill mould with a large area open to the atmosphere was used, the bottom being a copper plate provided with water-cooling. The copper was not affected by the stream of steel as long as this did not strike continuously

at one place, and provided it was covered with a thin layer of "chill-mould grease." An almost flat surface with no pipe was obtained. No information on the mould dimensions or ingot weight are given.

**The Examination of a Rimming-Steel Ingot Containing 0·29% of Carbon.** T. Swinden. (Iron and Steel Institute, 1944, this Journal, Section I). A 2½-ton ingot of rimming steel containing 0·29% of carbon was examined with particular reference to carbon distribution. There were significant differences in the behaviour of this steel as compared with low-carbon rimming steel during solidification, but nevertheless the heterogeneity was of the same general character. The rim contained about 0·25% of carbon, and, in answer to previous suggestions on the point, it is submitted that this could not have been deposited as primary crystals of δ-iron.

**Rimming Steel.—Experiments on Melts of Rimming Steel Composition in the Laboratory High-Frequency Furnace.** T. Swinden, W. W. Stevenson and G. E. Speight. (Iron and Steel Institute, 1944, this Journal, Section I). Using a small high-frequency melting unit (nominal capacity, 18 lb. of metal), experiments were conducted in an endeavour to reproduce the conditions prevailing during the freezing of commercial rimming-steel ingots. Owing to the small mass of material involved this was not completely possible, but some interesting observations were made. A noticeable feature was the invariable appearance of a thick crust of pure "rim" at the top of the ingots.

## FORGING, STAMPING AND DRAWING

(Continued from pp. 151 A-155 A)

**Forging Die Design.** J. Mueller. (Steel Processing, 1943, vol. 29, Dec., pp. 627-628). Recommendations on forging die design are made and diagrams of three stages in the forging of hinges are presented with explanatory notes.

**The Determination of Stress in Drop Stamps.** A. Blainey. (Engineer, 1944, vol. 177, Feb. 11, pp. 104-106; Feb. 18, pp. 125-126; Feb. 25, pp. 144-146). It is shown how to determine the stresses produced in the various components and in the foundations of drop stamps, and in stamping dies. For this purpose measurements were made of the deceleration of the tup, the acceleration and deflection of the anvil and ground, and the decrease of die-to-die distance, during stamping, in the case of several large pneumatic and drop stamps. The values of tup deceleration were found to be of the order of 2000 and 3000 times gravity, from which the maximum stresses occurring in the tup and piston rod were

estimated and shown to approach the yield strength of the steel. A method is proposed for reducing these stresses. The maximum die-to-die force in large stamps was estimated to be 50,000–60,000 tons weight, and from this the stresses in stamping dies were calculated and shown to exceed the yield strength of the material. The maximum stress in the base timbers was estimated from the values of anvil deflection and the period of oscillation of the whole stamp on its resilient support. Curves showing ground deflection (earth tremor) at increasing distances from drop stamps can be used to determine suitable positions for precision grinding machines where vibration should be at a minimum.

**Steel Processing—Producing Tubular Railway Axles at Pittsburgh Steel Company.** (Steel Processing, 1943, vol. 29, Dec., pp. 623–626). **Tubular Railway Axles—A Product of Pittsburgh Steel Company.** (Blast Furnace and Steel Plant, 1943, vol. 31, Dec., pp. 1376–1378). The process of making tubular railway wagon axles by piercing, rolling and upsetting is described (*see p. 126 A*).

**The Making and Testing of Steel Cylinders for Compressed Fuel Gas for Internal Combustion Engines.** C. Berthelot. (Revue de Métallurgie, Mémoires, 1942, vol. 39, Aug., pp. 247–255; Sept., pp. 265–279). A review is presented of the requirements of steel cylinders for compressed coal gas for fuel for automobiles in France, and the methods of manufacturing and testing them.

**Determining Defects in forgings.** G. Sachs. (Steel, 1944, vol. 114, Jan. 24, pp. 60–61). A comprehensive table is presented which contains a list of many types of defects in forgings and their probable causes.

**Cold Forging.** J. A. Stewart. (Australian Institute of Metals : Australasian Engineer, 1943, vol. 43, Nov. 8, pp. 17–22). An account is given of the cold-heading process with particulars of the types of machines, the principles of operation, the design of the tools, the materials which can be headed, some applications of the process, and the heat treatment of cold-headed bolts.

## ROLLING-MILL PRACTICE

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(Continued from pp. 155 A–157 A)

**Bar Mills and Bar Mill Roll Design.** R. E. Beynon. (Iron and Steel Engineer, 1943, vol. 20, Dec., pp. 40–68). The various stages in the development of bar mills in the United States and in Europe are described with the aid of 28 drawings of different layouts. The design of furnaces, millstands and hot beds, and the casting of bar-mill rolls are reviewed. In the concluding part, roll design is discussed and 30 drawings of the passes to produce various sections are given.

**Some Observations on Plate Mills.** W. A. White. (Iron and Steel Engineer, 1944, vol. 21, Jan., pp. 29-33). After some notes on the trend of plate-mill design in the United States, a description is given of the new plate mill at the Fontana Works of Kaiser Company, Incorporated. This is a 110-in. two-stand tandem mill consisting of a two-high roughing stand and a three-high finishing stand with the necessary tables, shears and levellers. It is designed to roll plates ranging from  $\frac{3}{16}$  to  $1\frac{1}{2}$  in. thick, up to 96 in. wide, at 45-60 tons per hr. from ingots ranging from 12 to 24 in. in thickness. The roughing stand rolls are 44 in. in dia. with a 3500-h.p., 750-V. reversing motor connected to each roll. The top and bottom rolls of the finishing stand are 40 in. in dia. and the centre roll is  $26\frac{1}{2}$  in. in dia. This stand is driven by a 7000-h.p., 750-V. motor. These stands are 100 ft. apart, and 27 ft. 6 in. in front of the roughing stand there is a vertical edging stand with rolls 44 in. in dia. and 30 in. high.

**Holding Tension with the Amplidyne.** H. W. Poole. (Blast Furnace and Steel Plant, 1943, vol. 31, Dec., pp. 1379-1380). A circuit diagram for amplidyne control of the tension reel motor for a strip mill is presented, and it is shown that amplidyne control is very suitable for this purpose because of its simplicity, speed of response, accuracy, ease of adjustment, stability and reliability.

**Strip Mill Rehabilitated while in Operation.** J. Farrington. (Iron and Steel Engineer, 1943, vol. 20, Dec., pp. 33-38). A description is given of the way in which the strip mill of the Wheeling Steel Corporation, Steubenville, was modernised so as to increase the delivery speed from 1200 to 1800 ft. per min., and the maximum strip width from 60 to 66 in. The mill, as originally laid out, had eleven stands, and the new mill has ten stands. In planning the change over, special attention was paid to limiting the time in which the mill would be out of production and the actual rolling time lost was only  $8\frac{1}{2}$  days.

## HEAT TREATMENT

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(Continued from pp. 159 A-163 A)

**German Emergency Steels and Their Treatment in Salt Baths.** C. Albrecht. (Schweizer Archiv : Metal Progress, 1943, vol. 44, Dec., pp. 1121-1123). A brief account is given of German methods for case-hardening and heat-treating chromium-manganese and silicon-manganese steels. Salt-bath carburising combined with a diffusion treatment is applied and enables the carbon content of the case to be closely controlled. Air convection furnaces are used to preheat the work to 500-800° F. prior to transfer into the hot salt bath. This is followed by quenching in oil, draining and

rinsing. An air furnace for preheating and a salt-bath furnace are also used for the subsequent tempering.

**The Theory and Practice of Industrial Electronic Heating.** J. P. Jordan. (*General Electric Review*, 1943, vol. 46, Dec., pp. 675-683). The term "electronic heating" covers the application of high-frequency vacuum-tube oscillators to the induction heating of metals and to the dielectric heating of non-metallic materials. The theory of electronic heating is explained with examples of circuit diagrams, and the apparatus required is described with recommendations on inductor coil design.

**Induction Heat Treating.** (*Steel Processing*, 1943, vol. 29, Dec., pp. 645-646). The equipment used for the induction hardening of the teeth of 12-in. dia. sprockets for tank tracks is described (see p. 161 A).

**The Use of Artificial Atmospheres in Heat-Treatment Furnaces.** M. Fourment. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, Apr., pp. 97-103). Descriptions are given of methods of preparing protective atmospheres for heat-treatment furnaces with several diagrams and illustrations of the plant required.

**Nitralloy Steels.** (*Automobile Engineer*, 1944, vol. 34, Feb., pp. 71-72). Some advantages of hardening by nitriding are pointed out and the properties of Nitralloy steels are discussed. Nitriding is carried out at 500° C., and there is no subsequent quenching; as a result, parts of very complicated design can be hardened without any appreciable distortion. The nitrided case retains its full hardness at temperatures up to 500° C. As a general rule parts can be finish-machined or ground from rolled Nitralloy steel bars in the oil-hardened and tempered condition.

**Short Anneal for Carburized 3312.** C. W. Dietz. (*Metal Progress*, 1943, vol. 44, Dec., pp. 1097-1100). Experiments on the annealing of steel S.A.E. 3312 so as to be able to machine it after carburising and before final hardening are described. This steel contains carbon 0·12%, manganese 0·45%, nickel 3·5% and chromium 1·5%. The procedure eventually adopted consisted of: (1) Cooling completely from the carburising temperature to room temperature by any convenient means provided that it is not extremely slow; (2) heating to 1380° F. and holding long enough for all parts to reach this temperature; (3) cooling to 1100° F. at any convenient speed (times varying from 50 min. to 6 hr. were tried with very little difference in the results); (4) holding at 1100° F. sufficiently long for all parts to attain this temperature; and (5) cooling to room temperature by any convenient means. The entire cycle need not take more than 8 hr.

**Sub-Zero Hardening Cycles.** G. B. Berlien. (*Steel*, 1944, vol. 114, Jan. 10, pp. 86-90). Some experiences with heat treatment and subsequent cold treatment at sub-zero temperatures of steel are related. It has been found difficult to trace the progress of the decomposition of austenite by refrigeration with the microscope,

and magnification at 2000 diameters would probably be required to reveal the very finely divided martensite. The examples of increased wear resistance obtained by cold treatment include high-speed, low-alloy, oil-hardening and stainless steels.

**Carbides in Low Chromium-Molybdenum Steels.** W. Crafts and C. M. Offenhauer. (*Transactions of the American Institute of Mining and Metallurgical Engineers*, 1943; vol. 154, pp. 361-373). Steels containing up to 1·5% of molybdenum without chromium and steels with up to 1% of molybdenum and 5% of chromium were examined to determine the nature of the carbide phases after quenching and tempering. Cementite was found in steels tempered at below 500-550° C., and carbides of the alloying elements were found after tempering at higher temperatures. These carbides included Cr<sub>7</sub>C<sub>3</sub> in intermediate chromium steels, Cr<sub>4</sub>C in higher chromium steels and Mo<sub>2</sub>C in molybdenum steels. All of these carbides were found in chromium-molybdenum steels. The approximate ranges of the carbides with respect to tempering temperature and composition are correlated in phase diagrams.

**The Hardening Quench.** E. Simister. (*Metallurgia*, 1944, vol. 29, Jan., pp. 115-118). The advantages and disadvantages of different cooling media for quenching steel are discussed. It is a disadvantage of water-quenching that the steel is cooled rapidly in the final stages, *i.e.*, when it is approaching the fully hardened condition. Raising the temperature of the water not only restricts the cooling rate through the critical range, but depresses the temperature at which cooling is fastest to a point where the steel is in its hardest condition, and so greatly increases the quenching stresses. Warm water is, therefore, not an ideal quenching medium ; it is liable to cause soft spots and increase the danger of cracking. The presence of a small amount of soap in an aqueous bath is most detrimental to its quenching properties, as it greatly extends the period during which vapour surrounds the part being hardened. The quenching ability of oil is little affected by moderate variations in the bath temperature ; generally speaking, oil baths function more efficiently if kept warm, 30-60° C. being the temperature range in usual practice. There must be an adequate volume and good circulation of the oil ; 1 gal. of oil for each 1 lb. of steel quenched per hr. is a good rule for deciding the tank capacity. A thin refractory wash or facing mixture applied to tool steel results in a greatly improved quench as it increases the cooling rate and reduces the initial vapour stage referred to above.

## WELDING AND CUTTING

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(Continued from pp. 131 A-134 A)

**Metallic Arc Welding of X-4130 Steel Tubing.** W. T. Tiffin. (Welding Journal, 1943, vol. 22, Dec., pp. 613-S-615-S). The results of tensile and hardness tests are reported on strips cut from electrically welded tubes of steel S.A.E. X-4130,  $1\frac{1}{4}$  in. in outside dia. with wall thicknesses of 0.049, 0.063 and 0.078 in. This is a chromium-molybdenum steel. A wide variety of current strengths were used to establish the conditions which produced the best weld from the point of view of ease and speed of welding, appearance and physical properties. As the current values increased the hardness gradients across the heat-affected zone decreased. At the position where the weld was started and finished the properties were much better than at the position half-way round, because the metal at the former position was heated and cooled twice, thus producing an almost normalised structure.

**Weldability Tests of Aircraft Structural Steels.** C. B. Voldrich and R. D. Williams. (Welding Journal, 1943, vol. 22, Nov., pp. 545-S-554-S). Tests are described for the evaluation of the weldability of air-hardening alloy steels used in aircraft construction. The tests are classified in four general groups, namely: (1) Hardness tests on the heat-affected parent metal; (2) ductility tests on the heat-affected metal; (3) strength tests on the welded joints; and (4) tests for hardness cracks in the heat-affected parent metal. Several types of hardness surveys are discussed; these give an incomplete and sometimes erroneous indication of weldability and should only be used in conjunction with other tests to assess weldability. Several ductility tests are described, but only the T-bend test gives a usable weldability index. Probably the best criterion of weldability is the occurrence of cracking in the heat-affected zone. No doubt a real relationship exists between the hardness, ductility and cracking tendency of the metal adjacent to the weld, but none of the tests described gives a reliable indication of this relationship. The circular weld-bead test promises to be a useful method for evaluating the cracking-sensitivity factor in relation to the analysis, processing and structure of the steel.

**An Electronic Circuit to Control Intensity and Timing of Power for Spot Welding.** W. B. Nottingham. (Review of Scientific Instruments, 1943, vol. 14, June, pp. 161-170). A welder control is described which can deliver currents as high as 200 amp. for any predetermined time from a fraction of a half-cycle of the 60-cycle power supply to 60 half-cycles. At any specific timing, the intensity may be controlled continuously from zero to its maximum value. The operation of the control depends on the co-ordinated application of two electronic circuits which individually or together have many other uses.

**The Fatigue Strength of Fillet-Weld Joints Connecting Steel Structural Members.** W. M. Wilson. (Welding Journal, 1943, vol. 22, Dec., pp. 605-S-612-S). The results of several series of fatigue tests on fillet-welded joints are described. Pairs of plates  $\frac{3}{8}$  in. thick and 9 in. wide at the ends were lapped over the ends of thicker plates 12 in. wide, and fillet-welded in position, each joint consisting of three plates. The position and length of the welds and the shape of the 9-in. wide ends being different for each series of tests. Additional tests were made on fillet welds joining channels to plates. The object was to determine the design of joint having the greatest fatigue strength. Diagrams of each joint are shown and the test results are given in tables.

**Effect of Peening Temperature on Weld Metal.** R. E. Somers. (Welding Journal, 1943, vol. 22, Nov., pp. 570-S-572-S). Tests are described in which Rockwell hardness readings were taken across welds in mild-steel plate to determine the effects of peening the weld metal at temperatures of  $70^{\circ}$ ,  $200^{\circ}$ ,  $400^{\circ}$ ,  $600^{\circ}$  and  $1200^{\circ}$  F. Peening in the "blue brittle" temperature range increased the hardness by 25%, the hardening being greater than that occurring in the heat-affected zone of the parent metal. Depositing another layer of metal on the peened layer has a beneficial tempering effect and has led to the practice of peening all but the last layer of a welded joint. Peening should not be done at below  $100^{\circ}$  F.

**Arc-Welded Stainless Steel Linings for Refinery Pressure Vessels.** W. W. McClow. (Chemical and Metallurgical Engineering, 1943, vol. 50, Nov., pp. 134-135). The technique employed for welding a stainless lining in an oil refinery pressure vessel 8 ft. 6 in. in dia. and 104 ft. high is described. The lining was made up of strips of No. 12 gauge 12-14% chromium steel 4 in. wide; these were placed in position  $\frac{1}{4}$  in. apart, and each joint was welded in two passes which also welded the strips to the  $1\frac{9}{16}$ -in. thick wall of the vessel.

**The Welding and Inspection of Pressure Vessels.** R. T. O'Donnell. (Australian Welding Institute : Australasian Engineer, 1943, vol. 43, Nov. 8, pp. 30-31, 48-53). The factors governing the strength and safety of welded joints in pressure vessels are discussed with particular reference to the position of welds joining end plates to shell plates and to the stresses on circumferential and longitudinal seams.

**Chain Cables.** T. Scott Glover. (Institution of Engineers and Shipbuilders in Scotland : Welding, 1944, vol. 12, Feb., pp. 91-98). The paper on the manufacture of stud link chain cables which appeared in Engineering, 1943, vol. 156, Dec. 10, pp. 477-480, is reproduced (see p. 91 A).

**Flame Cutting Heavy Sections and Large Diameters.** R. L. Deily and E. Benyo. (Welding Journal, 1943, vol. 22, Dec., pp. 1006-1016). **Heavy Gas Cutting.** R. L. Deily and E. Benyo. (Steel, 1943, vol. 113, Dec. 13, pp. 110-111, 118-120). The equip-

ment and procedure for the oxy-acetylene cutting of steel of heavy section are described. It is essential to provide for an adequate and continuous supply of oxygen at high pressure for the work in hand and to make sure it is properly preheated, employing a second torch for this if necessary. The cutting of a marine engine crank-shaft from a block of steel 42 in. thick is described.

**High-Production Flame Cutting.** H. Lawrence. (Steel, 1944, vol. 114, Jan 24, pp. 58-60, 90). Some of the oxy-acetylene cutting equipment at the works of the By-Products Steel Corporation, Coatesville, is described. Several multi-burner machines are used. Oxygen is obtained in liquid form and, after evaporation, the gas is supplied to conveniently placed points at 150 lb. per sq. in. One machine with four burners simultaneously cuts four identical sprockets out of heavy steel plate from a single template.

## CLEANING AND PICKLING OF METALS

(Continued from pp. 163 A-164 A)

**Cleaning and Descaling Steel by Electrolytic Pickling in Molten Caustic Soda.** N. L. Evans. (Iron and Steel Institute, 1944, this Journal, Section I). It is claimed for the process of cleaning and descaling steel by electrolytic treatment in molten caustic soda that it produces a highly satisfactory surface for subsequent operations such as plating, galvanising, tinning, vitreous enamelling, painting, &c. It imparts to the steel a mild degree of resistance to rusting, and hydrogen is not absorbed as in certain other scale-removal methods. Metallic losses are minimised and the consumption of chemicals is low. The present investigation is concerned mainly with finding the optimum conditions of time, temperature and current density, and with the occurrence and prevention of brown stains on the work. Certain electrical conditions in the plant have been investigated, and their bearing on plant design is discussed. Several other matters relating to the plant are dealt with, including precautions necessary for safe operation, methods of removing sponge iron from the treated metal surfaces, methods of heating the caustic soda, and the method of collecting and removing sludge from the tanks.

## PROPERTIES AND TESTS

(Continued from pp. 169 A-174 A)

**A New Type of Recording Dilatometer.** W. E. Kingston. (Metal Progress, 1943, vol. 44, Dec., pp. 1115-1120). A detailed description is given of a recording dilatometer which was developed

for studying low-expansion metals and alloys. The concentric quartz-tube principle as used by the United States Bureau of Standards is applied in conjunction with a recording potentiometer controller with the time-drive mechanism removed and replaced by a shaft from the dial gauge to the chart roll drive. An accurate dilation-temperature curve is thus directly obtained. The complete apparatus is made up of six co-ordinated units, namely, an electric furnace, concentric quartz tubes, dial gauge standard and dial gauge, contact mechanism, transmission shaft, recorder and electronic relay.

**A Fatigue-Testing Machine for Caquot Test-Pieces.** R. Guillery. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, Jan., pp. 27-29). A description is given of a fatigue-testing machine to take specimens of the type "Air-830" standardised by the Services de l'Aéronautique. In this machine, which is designed to shorten the time required for testing fairly soft materials, the specimen is submitted to alternating bend tests at 6200 cycles per min.

**Further Experiments on the Damping Capacity of Metals.** W. H. Hatfield, L. Rotherham and E. M. A. Harvey. (*North-East Coast Institution of Engineers and Shipbuilders*, Mar., 1944, Preprint). Since the previous report on damping-capacity experiments was published (see *Journ. I. and S.I.*, 1942, No. II., p. 70 A) further tests have been carried out. The effects of a long period of service and of continuous testing up to a period of a week have been investigated, no effect outside the limits of experimental error having been detected. The reproducibility of results from a number of samples from the same bar of 0.12% carbon steel was very good, whilst that between different casts of the same material was not so marked. Small variations in temperature, of the type encountered in the normal fluctuations of room temperature, were very important with 0.12% carbon steel, quite marked with 18/8 stainless steel, and unimportant with stainless iron. Fairly good correlation was obtained when damping capacity was plotted against the carbon content of the carbon steels, the degree of correlation being highest when the samples were obtained from approximately the same size of bar, and were in the same heat-treated condition. Interesting results were obtained from the series of chromium steels tested. The first four steels of the series (containing 2.16%, 5.39%, 8.50% and 11.44% of chromium respectively) all of which exhibited the same type of microstructure, showed an increase of damping capacity with increasing chromium content up to 8.5%, the values for the 8.5% and 11.44% chromium steels being identical within the limits of error of the experiment. The high values for these last two steels indicate that the values recorded for the stainless irons and stainless steels are not anomalous, but are dependent on the composition of the material, or on some other factor which itself varies with the composition. The relatively low values of the high-chromium stainless iron and of the 21% and 33% chromium

steels gave further evidence of the shape of the curve plotted between damping capacity and chromium content. A successful attempt was made to correlate damping capacity with magnetostriction for the series of iron-nickel alloys. When the sign of the numerical coefficient of magnetostriction is neglected, the shape of the magnetostriction curve is followed closely by the damping-capacity curves. The influence of defects on the damping capacity of materials was noted. In both the cases studied, the cracked specimens gave higher values of damping capacity than those without cracks. The greater difference observed with the specimens of 3·5%-nickel chromium steel was probably due to the greater number of defects present. Magnetic-etching of the defective specimens from both the 3·5%-nickel chromium steel bar and the 3·25% nickel steel forging had indicated that a larger number of defects were present in the former than in the latter. The addition of extra sulphur to an ingot of a 3·5%-nickel chromium-molybdenum steel caused an increase in damping capacity. Similar additions of sulphur to corrosion-resisting materials caused little change in the values of damping capacity recorded. A few experiments carried out on 0·13% carbon steel to assess the effects of cold work show that, with this material, the result of cold work is to decrease the damping capacity. After retempering in the laboratory, the values of damping capacity of all these materials were increased. Tests on a 0·33% carbon steel specimen with three different finishes indicated that variations in surface finish do not affect the values of damping capacity recorded. Meehanite gave further estimates of the degree of reproducibility obtainable both between casts and within a cast. The values of damping capacity recorded for this material, which is a type of cast iron, were lower at all stresses than the corresponding values for the other cast irons reported in the earlier paper.

**Effects of Some Elements on Hardenability.** W. Crafts and J. L. Lamont. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1657 : Metals Technology, 1944, vol. 11, Jan.). Experiments to determine the manner in which silicon, aluminium and manganese affect the hardenability of steel have already been reported (*see* Journ. I. and S.I., 1943, No. II., p. 32 A). In the present paper the results of investigations of the effects of nickel, chromium, molybdenum, zirconium, vanadium, titanium and boron are given ; these are reduced to the form of hardenability multiplying factors for calculating the ideal critical diameter according to Grossmann's principle (*see* Journ. I. and S.I., 1942, No. II., p. 219 A). The elements usually classed as deoxidisers (titanium, vanadium and zirconium) increased the hardenability in about the same proportion as the carbide-forming elements chromium and molybdenum. The effect of boron on hardenability did not appear to be influenced by the amount of alloying element in the steel.

**Effect of Several Variables on the Hardenability of High-Carbon Steels.** E. S. Rowland, J. Welchner and R. H. Marshall. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1662 : Metals Technology, 1944, vol. 11, Jan.). The investigations reported in this paper are supplementary to earlier work by J. Welchner, E. S. Rowland and J. E. Ubben on the effects of quenching temperature, holding time and prior structure on the hardenability of alloy steels (see p. 103 A). A plain carbon hypereutectoid steel, a 1% carbon steel containing 1.44% of chromium and 0.36% of nickel, and a molybdenum-bearing high-carbon steel containing some graphite were used in the present work. The effects of holding times up to 4 hr. and quenching temperatures from 1450° to 1700° F. on the end-quench hardenability values of these steels hardened from the normalised and from the spheroidised states were determined. The hardenability changes produced in a given analysis by variation in time, temperature and prior structure are predictable from a knowledge of the rate of carbon solution from the prior structure used, the grain size and the number and distribution of nucleating carbides. The additional factor of the concentration gradients of the alloying elements is probably of minor importance. Micrographs supply evidence that a definite relationship exists between the number and distribution of visible carbides in the quenched structure of a given hypereutectoid steel and the hardenability test result, in that the conditions that produce higher hardenability also leave fewer visible carbides in the microstructure. Such evidence points to the existence of a definite relationship in a given steel between the number and distribution of visible carbides and the corresponding number and distribution of submicroscopic carbides that may actually act as nuclei for austenite decomposition on quenching.

**Aging and the Yield Point in Steel.** J. R. Low, jun., and M. Gensamer. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1644 : Metals Technology, 1943, vol. 10, Dec.). Experiments are described the results of which support the view that pure iron should not have a marked yield point nor exhibit strain-ageing, and that carbon and nitrogen are primarily responsible for these two characteristics of commercial steels, whilst oxygen is relatively unimportant. Rockwell hardness and tensile tests were made on specimens of low-carbon basic open-hearth steel strip of deep-drawing quality and the changes in these properties after annealing in wet hydrogen were observed. The yield point and the strain-ageing and quench-ageing effects can all be eliminated in low-carbon steels by short-time annealing at about 700° C. in wet hydrogen. The time required to effect this increases with the thickness of the metal and the initial carbon content. The time decreases with increasing temperature up to about 740° C., with increasing proportions of water-vapour in the hydrogen and with faster rate of flow of the gas over the metal. The elimination

of the yield point and of ageing is due to the removal of carbon or nitrogen or both, and if either of these elements is reintroduced, both phenomena will reoccur. The presence of either carbon or nitrogen in amounts up to 0·003% is sufficient to produce both yield point and ageing. The literature is reviewed and a bibliography of 100 references is appended.

**Factors Affecting the Ductility of Cast Steel.** G. A. Timmons. (*Transactions of the American Foundrymen's Association*, 1943, vol. 51, Dec., pp. 417-480). The manner in which porosity, non-metallic inclusions, temper brittleness and the distribution of the austenite decomposition products affect the ductility of cast steel are discussed. Any factor which tends to raise the resistance to flow in relation to the resistance to cohesive failure will tend to reduce the ductility of a steel casting. The solidification pattern and the degree of segregation of alloying elements, which are dependent upon the rate of solidification, exert an important influence upon the ductility of a steel casting at a given hardness, chiefly through their effects upon hardenability and the distribution of the microconstituents. When a steel is highly segregated, its hardenability is lower than that of a steel of the average composition and a faster rate of cooling will be required to produce full hardening. If the critical quenching rate is not exceeded upon cooling from the austenitic state, regions rich in the alloying element will generally transform at temperatures lower than those at which transformation will take place in the regions less rich in alloying elements. The resulting structure will therefore consist of two or more microconstituents varying in their mechanical properties and distributed in a pattern which resulted from the "coring" which took place during solidification. If the harder structure is distributed in a network pattern, or in any manner which breaks up the continuity of the softer more ductile matrix, plastic deformation in the latter will be restricted and the resistance to flow will be appreciably increased with respect to the resistance to fracture. The steel in this condition will be susceptible to failure in a brittle manner and will be less fit for service applications in which high concentrations of three-dimensional stress may prevail, or where the rate of load application is moderately high. In order to obtain the maximum ductility at any given hardness, the steel must be quenched from the austenitic state at such a rate that it will be fully martensitic by the time it has reached room temperature. The facts that in normalised castings of some alloy steels, a matrix of Widmannstätten structure with a network of martensite may be formed as a result of "coring", and that this structure possesses low ductility, indicate that a considerable improvement in the mechanical properties of large castings may be realised by employing the principles of isothermal transformation by which the transformation in all parts of the casting is forced to take place at one temperature. For such treatment, a steel need have only

sufficient alloying element added to prevent decomposition of the austenite at temperatures above the nose of the S-curve when cooled at the rate prevailing in the given section size together with a uniform distribution of carbon in the austenitic state.

**The Structure of Cast Steel. Brittleness and Intergranular Fracture.** H. Jolivet. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, Aug., pp. 233-246; Sept., pp. 257-264). Brittleness, characterised by intergranular fracture, which is not removed by annealing, has been observed in some special cast steels. Reduction by rolling tends to remove this condition and improves the properties in the longitudinal direction more than in the transverse direction. A study of the solidification of such steels in the  $\delta$ -phase has shown that the brittleness is due to a lack of cohesion between the austenite grains, or the secondary structure, which has no relation to the dendritic segregation. The cause of this is the precipitation of either cementite or non-metallic particles in the austenite grain boundaries. Subsequent heat treatment does not affect the non-metallic inclusions, but it homogenises any heterogeneous dendritic structure.

**Tool Steels for Working Hot Metals.** H. Treppschuh. (Iron and Steel Institute, Dec., 1943, Translation Series, No. 159). An English translation is presented of a paper on the properties of steel for dies, mandrels and other tools for working hot metals. The article appeared originally in *Stahl und Eisen*, 1943, vol. 63, Mar. 11, pp. 189-199 (*see Journ. I. and S.I.*, 1943, No. II., p. 33 A).

**The Hot Elongation Properties of Steels Loaded in Tension.** J. de Lacombe. (*Revue de Métallurgie, Mémoires*, 1942, vol. 39, Apr., pp. 105-111; May, pp. 152-158; June, pp. 181-188). Apparatus is described with which time-elongation curves were obtained on steel specimens loaded in tension at temperatures in the 380-800° C. range. Low-carbon steels with and without molybdenum, chromium-molybdenum steels, nickel-chromium-molybdenum steels and austenitic nickel-chromium steels were tested. Changes in length of the order of  $10^{-3}$  mm. were recorded photographically without difficulty. Most of the tests were run for periods of 25-35 hr. The curves obtained were subjected to a mathematical analysis by a method explained in a previous paper (*see Journ. I. and S.I.*, 1939, No. II., p. 214 A). The main part of the present paper contains a mathematical analysis of the test results in which the possibility for extrapolating them for periods up to 10,000 hr. is closely examined. It is concluded that in most cases tests lasting 1000 to 2000 hr. would be necessary to obtain data for extrapolation to 10,000 hr. The effects of temporary removal of the load were also studied.

**Preface to Diffusion.** R. F. Mehl. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1658 : Metals Technology, 1944, vol. 11, Jan.). This paper comprises the introductory address to the Symposium on Practical Aspects

of Diffusion held at the Chicago Meeting of the American Institute of Mining and Metallurgical Engineers in October, 1943. The theory of the physical factors determining the value of the diffusion constant  $D$  in various solid solutions is in a primitive state, as it does not go further than to state that  $D$  is the greater the farther the solute is from the solvent in the periodic table, *i.e.*, the greater the chemical affinity between solute and solvent. The rise of  $D$  to very high values near the limit of solid solubility is a striking phenomenon, but its meaning is uncertain, for the suggestion that the variation of  $D$  with concentration originates in the variation of the thermodynamic activity coefficient with concentration hardly seems acceptable on either scientific or factual grounds. Further research on the effect of grain size upon diffusion rates and on diffusion in single crystals is required.

#### The Influence of Gas-Metal Diffusion in Fabricating Processes.

F. N. Rhines. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1645 : Metals Technology, 1944, vol. 11, Jan.). A survey is made of the beneficial and detrimental ways in which the diffusion of gases in metals affects metal-fabricating processes. Metals become "gassed" more rapidly when they are overheated; this may be caused by increased solubility of the gas, more rapid diffusion, and/or a greater proportion of the gas being in the atomic state. Most metals appear to absorb hydrogen more rapidly from water-vapour than from hydrogen gas itself, probably because nascent hydrogen is released in contact with the metal when a metal oxide is formed by the oxygen of the water molecule. There are two common methods of removing gases dissolved in metals. One is by "fluxing" with an insoluble gas, an example of which is the bubbling of chlorine through aluminium to remove hydrogen. The second method involves slow freezing of the metal with stirring. Although most kinds of ingots contain some gas, either in minute cavities or blowholes, sound wrought products can usually be made from the ingot. Small quantities of hydrogen may remain in steels even after short treatments at relatively high temperatures. A special case of internal oxidation is the behaviour of silver-coated steel when heated for protracted intervals in air at temperatures as low as 425° C.; oxygen diffuses through the silver coating and reacts with dissolved iron in a zone within the silver. Iron and iron alloys absorb small quantities of nitrogen from the air and this decreases the rate of the decomposition of the austenite especially in the nickel-chromium austenitic steels. Atomic nitrogen diffuses rapidly into iron at slightly elevated temperatures and produces unstable compounds, greatly increasing the hardness of the metal.

#### A Micrographic Study of the Cleavage of Hydrogenized Ferrite.

C. A. Zapffe and G. A. Moore. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1943, vol. 154, pp. 335-352). The literature on the hydrogen embrittlement of

steel has pointed to the existence of crystal substructures of the mosaic type, but no clear conception of the actual nature of the crystal fragments and openings in the steel has yet been obtained. An account is given of a micrographic investigation of the surfaces upon which failure by cleavage has been caused by the presence of hydrogen. Ferrites of three different origins were first rendered ductile by purification in hydrogen with a subsequent treatment *in vacuo*, and were then embrittled by the addition of hydrogen alone. The flat cleavage facets formed when the hydrogen-treated ferrite suffered brittle fracture, unaffected by etching or polishing, were examined and the discontinuities utilised and affected by the gas were revealed in great detail. Examples are shown of structures ranging in size from the grain itself down to the limits of resolution of the microscope. The occlusion of hydrogen by iron at ordinary temperatures occurs as the retention of fluid compressed gas within microscopic openings, or rifts, into which the gas precipitates from supercooled or supersaturated solid solutions. Failure occurs by direct cleavage through these rifts. The action of slip is restricted in this structure either by the action of triaxial tensile forces reacting against the pressure of the occluded gas, or by the fact that the rifts cut the structure into fragments too small to experience internal slip under the forces available, or by the co-operation of both mechanisms. The rifts constitute internal surfaces within the grains and are of two types which the authors call the "lineage" and the "mosaic." The lineage is a continuous structure composed of branches in angular disarray. Some rifts form on or through this structure within which only a small number of true openings can be observed. The lineage discontinuity thus appears as a change of orientation without visible disjunction and the total rift volume appears to be comparatively small. The mosaic is a structure of small particles or blocks of more or less regular crystallographic form; these blocks are separated by disjunctions which probably make up the largest proportion of the total rift volume.

## METALLOGRAPHY AND CONSTITUTION

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(Continued from pp. 137 A-138 A)

**A Bibliography of Electron Microscopy.** C. Marton and S. Sass. (*Journal of Applied Physics*, 1943, vol. 14, Oct., pp. 522-531). A comprehensive bibliography of electron microscopy is presented; it is in eight sections as follows: (1) Books; (2) emission microscopy; (3) transmission type microscope; (4) optics of the transmission type electron microscope; (5) image defects; (6) electron speeds at above 100 kV.; (7) different related instruments; and (8) applications of the transmission type microscope.

**The Electrolytic Polishing of Metals for Microscopical Investigations.** L. von Hámos. (Iron and Steel Institute, 1944, Translation Series, No. 167). An English translation is presented of a paper describing an electrolytic method for preparing absolutely stress-free surfaces on steel, copper, brass, aluminium and white metal. The original appeared in Jernkontorets Annaler, 1942, vol. 126, No. 12, pp. 568-590 (see Journ. I. and S.I., 1943, No. I., p. 221 A).

**Electrolytic Polishing of Metallographic Specimens.** L. A. Hauser. (Iron Age, 1944, vol. 153, Jan. 20, pp. 48-54). A detailed description is given of the electrolytic polishing procedure which has been used successfully for two years by the Crucible Steel Company of America. Any one of the following three electrolytes is recommended : (1) 68-72% perchloric acid 185 c.c., acetic anhydride 765 c.c. and water 50 c.c.; (2) one volume of 68-72% perchloric acid with four volumes of ethyl alcohol denatured with ether; and (3) one volume of 68-72% perchloric acid with ten volumes of glacial acetic acid. Extreme care must be taken in the preparation of solution (1) to prevent explosion. Solution (2) also requires care but it can be made up in about 30 min. as compared with 5 or 6 hr. for solution (1). There is no danger with solution (3). Solutions (1) and (3) are suitable for plain carbon and low-alloy steels. The specimen is made the anode and a corrosion-resistant steel strip  $6 \times 2 \times \frac{1}{8}$  in. is made the cathode. For plain carbon steels the e.m.f. is 50-60 V., the current 1.5-2.5 amp., and the time required is 0.5-2 min. Some micrographs of the polished surfaces obtained are reproduced.

**Interference-Band Inspection of Surface Finish.** (Engineering, 1944, vol. 157, Mar. 17, pp. 205-207). A new method of examining surface finish on metals is described. It is based on the phenomenon of interference in which the rays of light reflected from two surfaces in close proximity interfere with one another, so that the uniform illumination imposed is broken up into bands either of colour or of dark and light alternately, according to whether white or monochromatic light is used. The procedure in this case requires a microscope suitable for magnifications up to at least 200 diameters, some cover-glasses about 15 mm. in dia. by 0.15 mm. thick, and a suitable light source. Certain filters are needed for white light. The cover-glass is placed over the metal surface and tilted at an angle between  $0.5^\circ$  and  $1^\circ$ . The resulting interference bands appear as equidistant parallel lines—straight if the surface is truly flat, and wavy or distorted if the surface deviates in any way from the flat.

**Quantitative Determination of Retained Austenite by X-Rays.** F. S. Gardner, M. Cohen and D. P. Antia. (Transactions of the American Institute of Mining and Metallurgical Engineers, 1943, vol. 154, pp. 306-317). An X-ray diffraction method is described for the quantitative measurement of retained austenite in heat-

treated steels. By means of an aluminium foil, which is exposed simultaneously with the steel specimen, a reference line is superimposed on the X-ray film along with the diffraction lines emanating from the steel. The ratio of the density of the austenite (200) $\alpha$  line to that of the aluminium (200) $\alpha$  line then becomes a direct function of the austenite content and is substantially independent of tube fluctuations, exposure time and the conditions of film development. The functional relationship between this density ratio and the percentage of retained austenite was established experimentally with the aid of 5%-nickel steels heat-treated to obtain various austenite contents. The austenite content was also determined independently by a metallographic point-counting procedure; the validity of this method was demonstrated by cross-checking with a photometric technique. Typical examples of the application of the X-ray method to 5%-nickel steels are given to show: (a) The effect of carbon content and cooling rate on the amount of retained austenite; (b) the course of the austenite decomposition during tempering; and (c) the austenite gradient in quenched steel due to decarburisation.

**Exposure Chart for Radiography of Steel.** H. R. Isenburger. (Metal Progress, 1943, vol. 44, Nov., p. 944 B). A group of three diagrams and a table are presented from which the correct X-ray exposure time can readily be determined for any thickness of steel up to 7 in., with film lengths of 6-24 in., focus-film distances of 12, 24, 28, 36 or 48 in., using a line-focus X-ray tube and pulsating D.C. equipment generating from 80,000 V. to 1,000,000 V.

**Direct Evidence of the Solubility of Ferrous Oxide in Pure Solid Iron.** R. Castro and A. Portevin. (Revue de Métallurgie, Mémoires, 1942, vol. 39, Aug., pp. 225-232). The solubility of ferrous oxide in pure iron at temperatures below the melting point of iron was studied by the microscopical examination of specimens measuring 10 mm. in dia.  $\times$  10 mm. long. These were prepared from melts of electrolytic iron with additions of pure ferrous oxide in a magnesia crucible heated in a high-frequency furnace. An apparatus was employed consisting of a vertical Pythagoras tube passing through a heating coil. The tube was exhausted by a mercury pump and the specimen was suspended inside it by a device which enabled it to be lowered from the coil into a quenching liquid after heating to the desired temperature. Micrographs of the same position before and after heating were obtained. Other specimens were examined before and after deformation by pressing at different temperatures. At temperatures below 700° C. ferrous oxide inclusions are less plastic than iron and their plasticity does not increase until the temperature is reached at which they become appreciably soluble in iron. After heating for 30 min. at 1000° C. the larger inclusions decrease in size and become more rounded. Most of the small inclusions disappear leaving black craters corresponding in size to that of the original inclusions.

**The Apparent Microstructure Produced by Hydrofluoric Acid Etching Reagents on Pure Iron and Iron-Silicon Alloys.** W. J. Wrażej. (Iron and Steel Institute, 1944, this Journal, Section I). The investigation of the etching of iron-silicon alloys as well as pure (electrolytic) iron and also plain carbon steel and cast iron shows that, in all cases, when hydrofluoric acid is used as the etching reagent, the surface of the micro-samples is covered with scars (etch markings). Such scars, called "barley-shell" markings, appear when iron fluoride formed during the etching has the opportunity to crystallise (*e.g.*, in the presence of alcohol or of alcoholic picric acid solution). Other etching reagents such as mixtures of hydrofluoric acid and nitric acid in alcoholic or glycerol solution act in exactly the same way. The crystal deposit formed during the etching is not removed when the samples are rinsed in alcohol. Washing the samples in water dissolves the crystal deposit and reveals the etching scars as the places where the crystals had been embedded. Thus, the scars have nothing in common either with the structure of the alloy or with its composition or condition. Examples are shown in the micrographs accompanying the paper. When etching with hydrofluoric acid in alcoholic solution bivalent iron fluoride ( $\text{FeF}_2$ ) is produced, of which the space group is different from those shown in the literature. To investigate this point X-ray examinations and chemical analyses were made. The salts ( $\text{FeF}_2$ ) obtained from iron-silicon alloy and from electrolytic iron appear to have the same structure, which is hexagonal indexed on orthohexagonal axes. The true hexagonal unit cell dimension would be  $c = a = 9.645 \text{ \AA}$ , the axial ratio being unity.

**The Nature of Martensite.** L. Guillet. (Revue de Métallurgie, Mémoires, 1942, vol. 39, Jan., pp. 12-19). The literature on the theories relating to the formation of martensite and its properties is reviewed. Data on its properties as investigated by X-ray, hardness testing and acoustic methods are presented. The conclusion is drawn that martensite consists of a supersaturated solid solution of iron carbide in  $\alpha$ -iron and that its high strength is explained by the distortion of its lattice by atoms of carbon.

**The Influence of the Various Elements upon the Position of the Eutectoid in the Iron-Carbon (Carbide) System.** C. L. Shapiro and J. Strauss. (American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1646: Metals Technology, 1943, vol. 10, Dec.). A critical examination is made of the theory that the amount of carbon necessary to form the iron-carbon eutectoid is lowered by the addition of any carbide-forming element. The conclusions of numerous investigators of ternary systems containing iron and carbon are quoted. The theory that all body-centered cubic carbide-forming elements reduce the carbon content of the eutectoid composition is not valid, for the only elements of this class conforming with this theory are chromium and tungsten, whereas vanadium, columbium and tantalum increase the carbon

content. Small amounts of molybdenum shift the eutectoid point to the left and large amounts move it to the right.

## ANALYSIS

(Continued from pp. 140 A-142 A)

**Modified Diffusion Pump for Analysis of Gases in Metals.** J. J. Naughton and H. H. Uhlig. (Industrial and Engineering Chemistry, Analytical Edition, vol. 15, Dec., pp. 750-751). A description is given of an improved form of two-stage mercury diffusion pump used in the analysis of gases evolved from metals heated in a high vacuum.

**Determination of Copper in Cast Iron by Direct Microelectrolysis.** W. M. MacNevin and R. A. Bourque. (Industrial and Engineering Chemistry, Analytical Edition, 1943, vol. 15, Dec., pp. 759-762). Experiments on the electrolysis of copper contained in solutions of iron in nitric acid showed that most of the difficulties disappeared when the determination was carried out with micro-apparatus and sufficient sample to give 0.003 to 0.002 g. of copper. A satisfactory procedure, taking about 30 min., for determining copper is described. Molybdenum is the interfering element commonly present; it deposits with the copper as the iridescent black sesquioxide. This is prevented by adding either phosphoric acid or ammonium bifluoride and some extra nitric acid.

**Spectrographic Determination of Nickel and Chromium in Stainless Steel.** J. H. Coulliéte. (Industrial and Engineering Chemistry, Analytical Edition, 1943, vol. 15, Dec., pp. 732-734). A procedure is described for the spectrographic determination of nickel and chromium in stainless steel. The analysis takes 9 min.; its accuracy is equal to that of wet methods, and it is recommended for controlling routine melting operations.

**Modern Methods for the Quantitative Spectrochemical Analysis of Alloys.** R. Castro. (Revue de Métallurgie, Mémoires, 1942, vol. 39, Feb., pp. 54-60; Mar., pp. 84-96; Apr., pp. 112-122). A comprehensive review is presented of spectrographic methods of analysing alloys. Separate sections deal with the choice of rays, photo-electric methods of measuring differences in line intensity, the analysis of alloys in solution and the elements to which spectrographic methods are applicable.

**Speeding up the Chemical Analysis of Miscellaneous Ferrous Alloys by Means of the Spectrograph.** W. H. Hammond and F. Fong. (Journal of the American Society of Naval Engineers, 1943, vol. 55, pp. 620-627). A comparison is made of the results obtained by standard A.S.T.M. wet methods of chemical analysis and spectrographic methods on specimens of chromium-vanadium

steel and of nickel-molybdenum steel. The analyses were carried out under American navy-yard laboratory conditions, where analyses have to be made as rapidly as possible before commencing ship's repair work. The results by the two methods were in good agreement; the spectrograph gave satisfactory precision and the results were obtained in a much shorter time. The carbon, phosphorus and sulphur cannot, however, be determined with the spectrograph.

**The Micro-Analysis of Solid Fuels. Part I. Proximate Analysis and Determination of Carbon Dioxide.** R. Belcher and C. E. Spooner. (Iron and Coal Trades Review, 1944, vol. 148, Jan. 21, pp. 79-80, 91). Micro-methods for the analysis of solid fuels are described and discussed. A sample of solid fuel must be pulverised to a size which will pass through a 120-mesh British Standard sieve so as to obtain a representative sample. A micro-method for the determination of moisture has been adopted in which the loss in weight of a sample placed in a tube maintained at 110° C. while a stream of dry nitrogen passes over it is determined. There are two methods available for determining the carbon dioxide in mine dusts. In the indirect method the material left after the ash determination is emptied into a silica flask and an excess of N/100 acid added; after boiling for 5 min. the excess acid is titrated with N/100 alkali. The method assumes that all the alkalinity is due to calcium oxide formed by decomposition of the carbonate, and on this basis the carbon dioxide is calculated. The direct method is due to F. E. Jones.

**The Mineral Matter of Coal and Coke.** R. A. Mott and C. E. Spooner. (Fuel in Science and Practice, 1944, vol. 23, Jan.-Feb., pp. 9-18). Several formulæ have been proposed to relate the amount of mineral matter in coal to the known amounts of ash, sulphur and other constituents. Wide usage is only possible if the calculation is applicable to analytical data readily obtainable in most laboratories, and is comparatively simple to make. In the present paper it is shown that this is possible. The mineral matter of coal is about 1·13 times the amount of ash, and, for comparative purposes, it is desirable to correct the calorific value, volatile matter, carbon, hydrogen and oxygen contents of coals to a dry mineral-matter-free basis. The chief factor in determining the ratio of mineral matter to ash is the water of hydration of the clay portion of the mineral matter. The second factor of importance is the conversion of iron pyrites to iron oxide, and subsidiary factors are the loss of carbon dioxide from carbonates and the loss of chlorine from metallic chlorides. Parr's formula for mineral matter and its application to the calculation of the calorific value, volatile matter, carbon and hydrogen can be simplified to forms which enable the calculation to be made quickly. The Parr formula has been adopted as standard for America and Canada, and it is suggested that it should be adopted as a general standard.

## SUBJECT INDEX.

[References to the papers read before the Institute are indicated by the word *Paper* following the page number. The letter *P.* denotes a reference in Section I. of the Journal which contains the reports of the proceedings of meetings, the papers read, and the discussions thereon. The letter *A.* denotes a reference to the section dealing with abstracts.]

*Indexing of Alloy Steels and Other Alloys.* In the indexing of alloy steels, carbon and iron are ignored and the alloying elements contained in the steel are arranged in alphabetical order; for example, all references to nickel-chromium-molybdenum steel will be found under the heading chromium-molybdenum-nickel steel. In the indexing of other alloys, carbon and iron, when present, are included in the title; iron, when present, is always mentioned first and the other elements follow in alphabetical order, carbon being in all cases mentioned last. Examples: "Iron-silicon-carbon alloys" and "iron-chromium-nickel-carbon alloys."

ABRASION. *See Wear.*

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